New *N*-Heterocyclic Carbene Ligands and Their Applications in Homogenous Catalysis

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For my Family, for their love and support.

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Zusammenfassung

Die Entwicklung von *N*-heterozyklischen Carbenen (NHCs) als Liganden für Übergangsmetallkatalysatoren hat zu vielen neuen Errungenschaften in der homogenen Katalyse beigetragen. Um die Familie von unterschiedlichen NHC Liganden zu erweitern, werden in der vorliegenden Dissertation folgende Ergebnisse präsentiert: (1) Eine Klasse von gesättigten NHC Liganden mit Naphthyl-basierten Seitenketten und ihre gute Performenz in drei unterschiedlichen katalytischen Reaktionen, und (2) eine Reihe von chiralen NHC Liganden, welche aus C_2-symmetrischen Diaminen mit Naphthylseitenketten dargestellt wurden, sowie die erfolgreiche Anwendung der entsprechenden Palladiumkomplexe in der asymmetrischen Synthese von Oxindolen mit quaternären Kohlenstoffzentren.

Das zweite Kapitel beschreibt die Synthese und Charakterisierung von leicht zugänglichen und stabilen NHCs, die mit Naphthyl in der Seitenkette substituiert sind. Bei der Anwendung in der Katalyse wurden exzellente Resultate in Palladium-basierten Kupplungsreaktionen, in der Ruthenium-basierten Metathese sowie in der organokatalytischen Ringöffnungsalkylierung von Epoxiden erhalten. Im dritten Kapitel wurde die Untersuchung der NHCs zum entsprechenden chiralen Gegenstück ausgeweitet indem die Chiralität von C_2-symmetrischen Diaminen für das heterozyklische Rückgrat genutzt wurde. Die zugehörigen Palladiumkomplexe mit diastereomerenreinen NHC Liganden wurden aufgetrennt und in der asymmetrischen Synthese von 3-Aryl-3-methyl-oxindolen getestet. Hierbei zeigten die katalytischen Daten einen drastischen Einfluss auf die Enantioselektivität je nach der Orientierung der Seitenkette. Das vierte Kapitel befasst sich mit einem anderen ähnlichen NHC Liganden, der die asymmetrische Synthese von 3-Allyl-3-aryl-oxindolen mit einer hohen Chemo- und Enantioselektivität begünstigen konnte.

Abstract

The recent development of *N*-heterocyclic carbenes (NHCs) as ligands for transition metal catalysts has proved to be very fruitful in the field of homogeneous catalysis. In order to expand the family of versatile NHC systems for catalysis, this dissertation presents: (1) a class of saturated NHC ligands with naphthyl-derived side chains and their good performance in three different types of catalysis, and (2) a series of chiral NHC ligands derived from C_2-symmetric diamines with naphthyl side chains and the successful applications of their palladium complexes in the asymmetric synthesis of oxindoles bearing quaternary carbon centers.

Chapter 2 describes the synthesis and characterization of a new class of easily accessible and stable NHCs which incorporate substituted naphthyl side chains. In catalysis, excellent catalytic results are obtained in palladium-based coupling reactions, in ruthenium-based metathesis, and in the organocatalytic ring-opening alkylation of epoxide. In Chapter 3, the NHC study was expanded to their chiral counterparts by introducing the chiral regime of C_2-symmetric diamines into their heterocyclic backbone. Palladium complexes bearing diastereomerically pure NHC ligand were separated and tested in the asymmetric synthesis of 3-aryl-3-methyl-oxindoles. The catalytic data demonstrates the dramatic effects on enantioselectivity according to the orientation of the side chains. Chapter 4 addresses another similar chiral NHC ligand which could promote the asymmetric synthesis of 3-allyl-3-aryl-oxindoles with high chemo- and enantioselectivity.

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Chapter 1

Introduction

What is a carbene? A carbene is an electron-deficient two-coordinate carbon compound with two non-bonding electrons. There are two states of carbenes according to the alignment of the two electrons: 1) ground state—the two unshared electrons are in the same orbital with antiparallel spins, also called singlet carbene; 2) excited state—the two electrons are in two different orbitals with parallel spins, also called triplet carbene) (Figure 1).

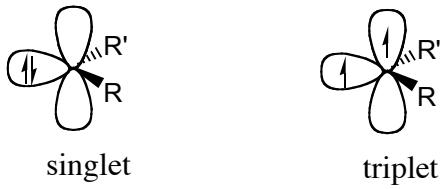


Figure 1. Singlet and triplet carbenes.

For a long time, carbenes were considered to be too reactive to be isolated, and the majority of carbene research was focused on transition metal carbene complexes. Metal carbene complexes are often classified into two types. The "Fischer carbenes", named after Ernst Otto Fischer, feature strong π-acceptors at the metal and are electrophilic at the carbene carbon atom.[1] "Schrock carbenes," named after Richard R. Schrock, are characterized by a more nucleophilic carbene carbon center; this species typically feature higher valent metals.[2] (Figure 2)

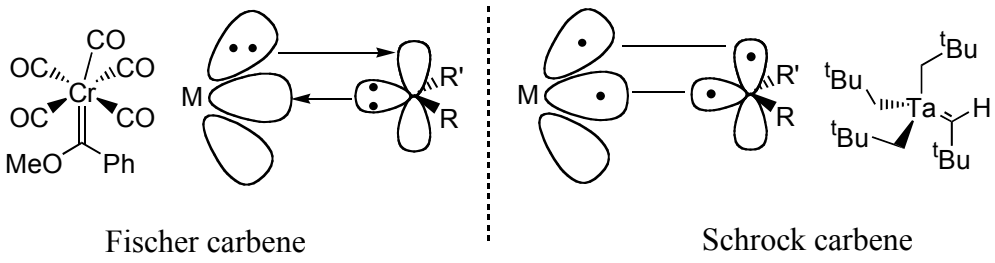
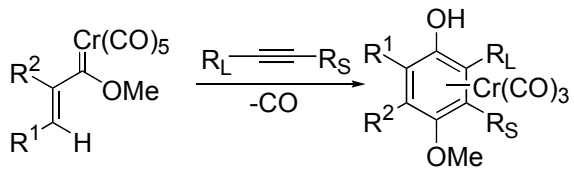


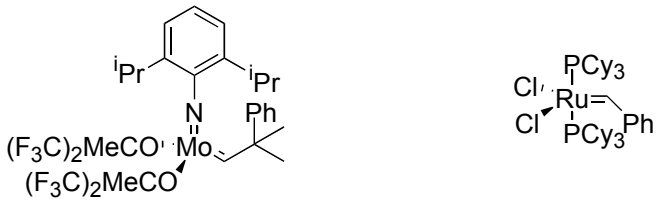
Figure 2. Fischer and Schrock carbenes.

Fischer carbene metal complexes have proven to be very efficient and extraordinarily versatile starting materials for carrying out a wide range of cycloaddition reactions, which give rise to a great array of aromatic and heterocyclic ring systems with a high degree of selectivity in most cases. For example, the Wulff-Dötz reaction is the chemical reaction of an aromatic or vinylic alkoxy pentacarbonyl chromium carbene complex with an alkyne and carbon monoxide to give a $Cr(CO)_3$-coordinated substituted phenol (Scheme 1).[3] The need to employ stoichiometric amounts of a Fischer carbene complex is, perhaps, the major drawback of these synthetically useful molecules and this has, most likely, been hampering their practical application in organic synthesis. Nevertheless, efforts to perform the chemistry of Fischer carbene complexes using catalytic amount of the metal are under way and some limited success has been achieved.[4]



Scheme 1. Wulff-Dötz reaction.

In contrast, Schrock carbene metal complexes have had a major impact in the field of catalysis. Especially valuable was the use of several Schrock carbene metal complexes for olefin metathesis, which opened up a new era of olefin metathesis and resulted in the 2005 Nobel Prize in Chemistry. Two research groups have mainly invented these catalysts: Schrock introduced tungsten and molybdenum alkylidene catalysts, which are commonly called "Schrock catalysts";[5] Grubbs developed ruthenium benzylidene catalysts, which are named as "Grubbs catalysts"[6] (Figure 3). These discoveries have triggered extensive follow-up work, and these achievements definitely represent a great treasure for the chemical community.



Schrock catalyst Grubbs catalyst

Figure 3. Typical Schrock catalyst and Grubbs catalyst.

Despite those advances in metal-carbene chemistry, it was not until 1991 that Arduengo et al. were able to isolate the first free carbene.[7] The free carbene unit was part of an *N*-heterocycle hence its name *N*-heterocyclic carbene (NHC). The free NHC IAd shown in Figure 4 is stable in the absence of oxygen and moisture, and could be handled easily being a crystalline, singlet, and electron-rich carbene. In comparison to a typical Fischer carbene, NHC–metal complexes contain the chemical bonding based on electron δ-type donation group of the filled methylene lone pair orbital to an empty metal d-orbital but no π electron back bonding of a filled metal d-orbital to the empty p-orbital on carbon, leaving a p orbital vacant. The lone electron pairs at the two adjacent nitrogen atoms could contribute to stabilizing the vacant orbital of the carbene center by formation of a three-center four-electron π system. Hence, a combination of σ-donor for the metal center and a π-acceptor for the two nitrogen atoms preserves the electron neutrality of the carbene center by an electronic push-pull mechanism. As a result, the bond between the metal and the NHC is usually presented as a single bond, which is quite unlike the double bond description in the Fischer and Schrock carbene metal complexes. This type of carbenes is stabilized both electronically and sterically, and offers great opportunity for other variations.

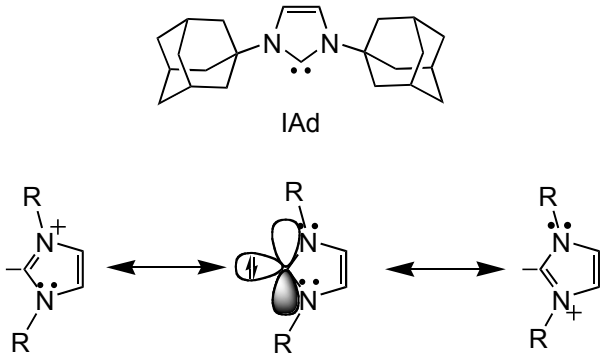


Figure 4. The first stable free carbene.

Indeed, the last decade has unimpeachably witnessed the fruitful use of N-heterocyclic carbenes (NHCs) as spectator or active ligands for transition-metal catalysts and as organic catalysts on their own (Figure 5).[8] Owing to their strong σ-donor and weak π-acceptor properties, NHCs have appeared as attractive and versatile alternatives to the ubiquitous tertiary phosphine ligands in many metal-catalyzed processes. In contrast to the extensively used phosphine complexes, most of the complexes formed with these ligands are stable towards heat, air, and moisture.[9] Indeed, N-heterocyclic carbenes are tightly bound to the meal, thereby avoiding

decomposition pathways or deposition of free (and inactive) metal under catalytic conditions.[10] These compounds were shown by infrared spectroscopy of their carbonyl derivatives to be very powerful σ-donors, even better than the most basic tertiary phosphines.[11] This, along with their easy steric modification, has resulted in intense research over the last decade. Nevertheless, truly viable and versatile NHCs are limited to monodentate aryl-substituted imidazol-2-ylidenes (2,4,6-mesityl-substituted IMes and 2,6-isopropylphenyl-substituted IPr) and their saturated imidazolin-2-ylidene counterparts (SIMes and SIPr) (Figure 6).

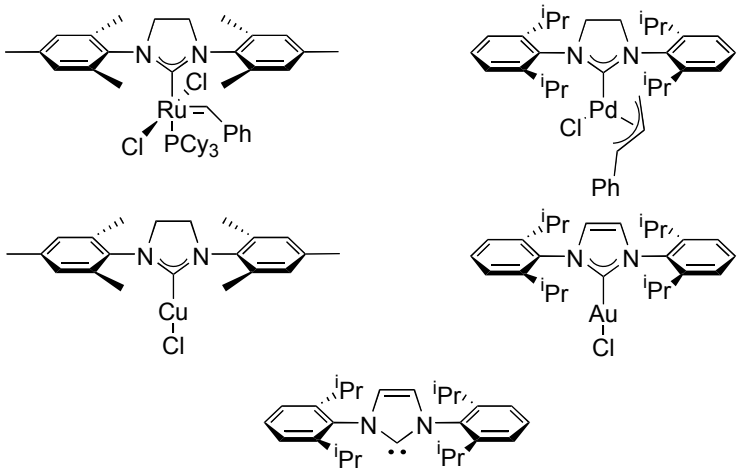


Figure 5. Examples of some successful catalysts using NHCs.

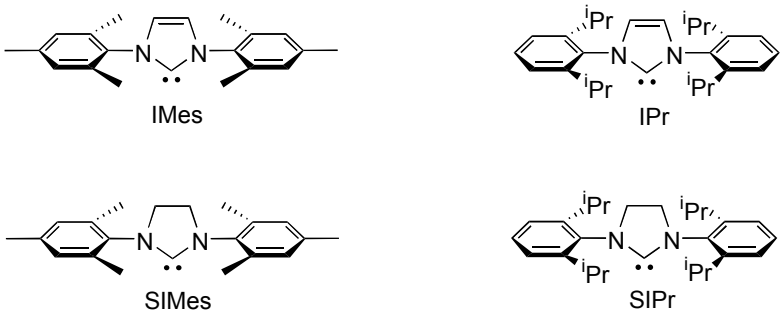
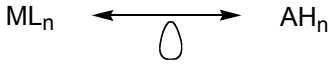


Figure 6. The most common NHCs.

To improve the understanding of chemical bonding in these metal complexes containing *N*-heterocyclic carbene ligands, the principle of isolobal analogy was incorporated.

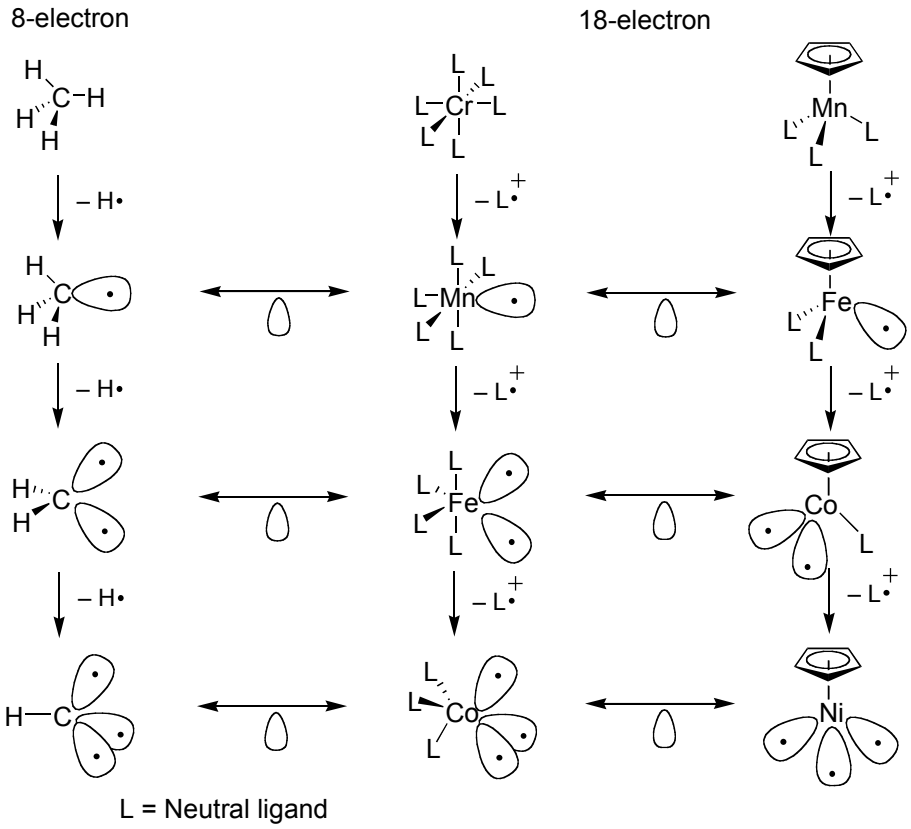
The isolobal analogy in organometallic chemistry proposed by Roald Hoffmann is recognized by half of the 1981 Nobel Prize in Chemistry,[12] and it aims to build bridges between the ML_n fragments from the inorganic world and the AH_n fragments in the organic world. Two fragments are deemed to be isolobal if the

number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar. The isolobal relationship is symbolized by a double-headed arrow with half an orbital below.



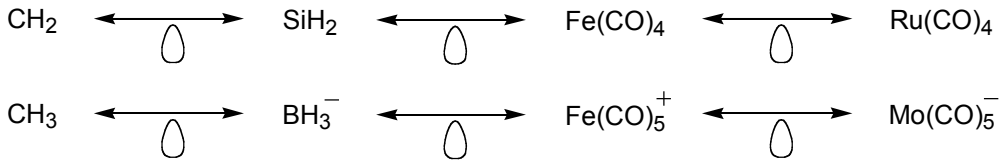
If two fragments are isolobal then they should have quite similar bonding capabilities. If molecules are isolobal then they should have very similar electronic structures. The isolobal analogy is helpful to provide simple ways to classify molecules and a short-cut to understand their electronic structures, to predict new hopefully stable molecules, and to offer clues about reactivity and reaction mechanisms.

The generation of isolobal fragments starts with saturated (molecules where all bonding and nonbonding MOs are filled and the antibonding MOs are empty) molecules of any sort. For example, main group fragments can be generated by starting from methane or any molecule obeying the octet rule; the transition metal fragments are generated in an analogous way, from the starting point of any molecule obeying the eighteen electron rule. A representative isolobal scheme generated by this approach is shown below (Scheme 2).

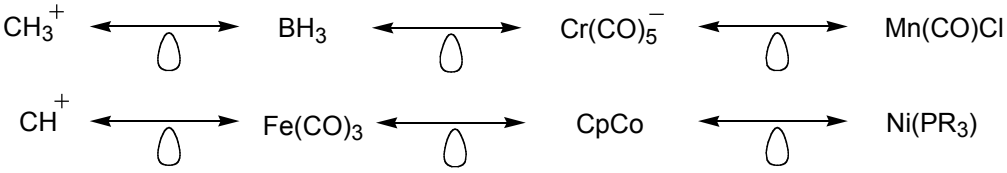


Scheme 2. Isolobal fragments.

The number of starting points is nearly infinite! One can also go up or down in the Periodic Table:



Furthermore, the number of electrons in the frontier orbitals can be adjusted to form other relationships:



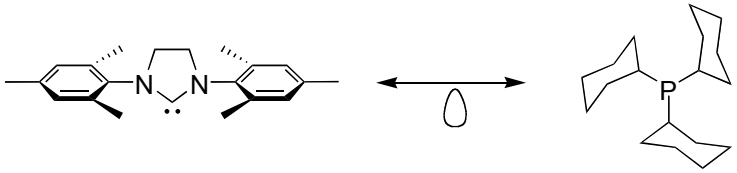
Due to Hoffmann's great contribution, the fundamentals of the isolobal analogy have now been exposed. Just how far reaching the relationships are, is shown below:

Table 1. Isolobal Analogies

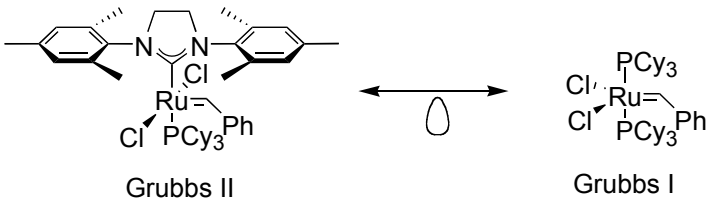
Organic	Transition Metal Coordination Number on which Analogy is Based				
Fragment	9	8	7	6	5
CH_3	d^1ML_8	d^3ML_7	d^5ML_6	d^7ML_5	d^9ML_4
CH_2	d^2ML_7	d^4ML_6	d^6ML_5	d^8ML_4	$d^{10}ML_3$
CH	d^3ML_6	d^5ML_5	d^7ML_4	d^9ML_3	

L = neutral two electron ligand

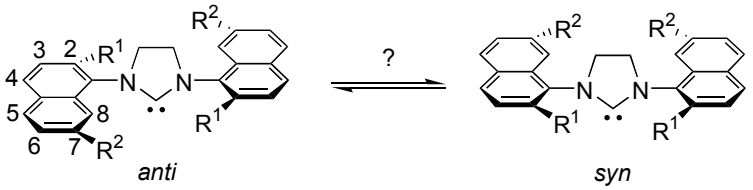
Based on the similar electronic structures of phosphine ligands (PR_3) and NHC ligands, they could be said to be isolobal. Therefore, they should possess very similar bonding capabilities towards metal centers, and NHC–metal bonds could be defined as single bonds in comparison with the well-accepted P–metal single bonds. Moreover, the parent metal complexes containing phosphine ligands and NHC ligands are also isolobal. Some examples are shown as follows:



SIMes $\qquad$ PCy_3



Development of new valuable NHC ligand architectures is a logical extension in this field. We therefore decided to target a new class of saturated, five-membered NHCs that bear two identical, modified naphthyl substituents at the two nitrogen positions. Due to the hindered rotation about the C–N bond, the incorporation of two naphthyl moieties should in principle give rise to two atropisomers with chiral C_2-symmetric (*anti*) and achiral C_s-symmetric (*syn*) conformations (eq 1). We reasoned that the fluxionality of the resulting ligands might be tunable by adjusting the size of the substituents at the 2- and 7-positions of the naphthyls. Once the barrier to rotation is high enough, the atropisomers would offer the potential for separation and resolution and could subsequently be used in catalytic enantioselective transformations. We also anticipated that complexation of NHCs to a metal center should increase the barrier to rotation in the atropoisomeric unit so that the isomers would, in principle, be separable at that stage.



The objective of the work described in this dissertation is to develop this new family of promising NHC ligands for homogeneous catalysis, especially for asymmetric catalysis.

In chapter 2, we outline the synthetic efforts that led to the development of this new class of NHC ligands together with an in depth analysis of their fluxional behavior. We also report rare examples of crystallographically characterized, saturated NHC compounds. Furthermore, we discuss their stability as monomers both experimentally and by using a newly developed computational method that allows one to predict monomer-dimer equilibria of NHCs.[13] Finally, we demonstrated the versatility of the new NHC ligands in metal-catalyzed reactions and as organocatalysts. Whereas palladium based systems investigated show comparable activity to Nolan's catalysts for C–C and C–N coupling reactions, all NHC ligands

studied outperform both SIPr•HBF_4 and phosphines in the base-catalyzed alkylation of internal epoxides. Excellent activity in ring-closing metathesis indicates that the naphthyl-based NHC architectures might indeed represent a good compromise between high reactivity with possibly better stability in metathesis reactions involving ruthenium complexes.

In chapter 3 and 4, we focus on expanding the new NHC family to chiral NHC ligands for asymmetric catalysis. Based on the chiral regime of C_2-symmetric starting diamines, the naphthyl-based chiral NHC ligands were readily prepared. Careful analysis of the NHC precursors showed the existence of three different isomers in such NHC structures. The NHC ligands were then transferred onto palladium while maintaining the isomeric ratio, which enabled us to separate these diastereomeric compounds via flash chromatography. Palladium complexes bearing diastereomerically pure NHC ligands were then tested in the asymmetric synthesis of 3-aryl-3-methyl-oxindoles and 3-allyl-3-aryl-oxindoles containing chiral quaternary carbon centers. The catalytic data demonstrate a dramatic effect on enantioselectivity depending on the orientation of the side chains. Satisfactorily, the biologically important oxindoles could be obtained with high enatioselectivity (up to 94% ee) when using these new NHC-Pd complexes.

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Chapter 2

Identification and Characterization of a New Family of Catalytically Highly Active Imidazolin-2-ylidenes

Xinjun Luan, Ronaldo Mariz, Michele Gatti, Chiara Costabile, Albert Poater, Luigi Cavallo, Anthony Linden, Reto Dorta*, *J. Am. Chem. Soc.* **2008**, *130*, 6848-6858.

2.1 Abstract

A new class of easily accessible and stable imidazolin-2-ylidenes has been synthesized where the side chains are comprised of substituted naphthyl units. Introduction of the naphthyl groups generates C_2-symmetric (*rac*) and C_s-symmetric (*meso*) atropisomers and interconversion between the isomers is studied in detail both experimentally and computationally. Complete characterization of the carbenes includes rare examples of crystallographically characterized saturated NHC structures. Steric properties of the ligands and an investigation of their stability are also presented. In catalysis, the new ligands show versatility comparable to the most widely used NHCs IMes/SIMes or IPr/SIPr. Excellent catalytic results are obtained when either the NHC salts (ring-opening alkylation of epoxides), NHC-modified Palladium compounds (C–C and C–N cross-couplings), or NHC–Ruthenium complexes (ring-closing metathesis) are employed. In several cases, this new ligand family provides catalytic systems of higher reactivity than observed with previously reported NHC compounds.

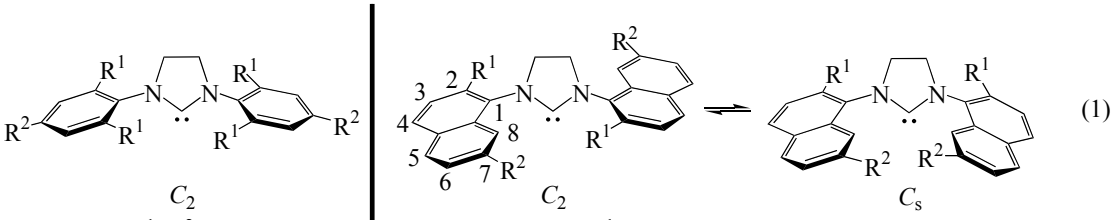
2.2 Introduction

The introduction of N-heterocyclic carbenes as ligands for transition metal catalysts and as organic catalysts on their own has put this class of compounds at the forefront of current research efforts.[1] Whereas hundreds of NHCs with various structural motifs have been synthesized and tested in catalysis, bulky, monodentate aryl-substituted imidazol-2-ylidenes (2,4,6-mesityl-substituted IMes and 2,6-isopropylphenyl-substituted IPr) and their saturated imidazolin-2-ylidene counterparts (SIMes and SIPr) still remain the only ligands that represent a truly viable alternative to phosphines, both in terms of versatility and reactivity. Presumably, the perpendicular arrangement of the aryl side chains, combined with the steric bulk on the aromatic rings, leads to a situation where these ligands confer stability to unsaturated and reactive metal centers during catalysis and where decomposition of the catalyst through unwanted metal–ligand interactions is rarely observed. Equally important for their widespread use and success is the simple fact that IMes/SIMes and IPr/SIPr are stable as free carbenes, making them easy to handle and manipulate. In this context, it is of note that most structures based on saturated imidazolin-2-ylidenes dimerize readily to give enetetramines. This renders saturated NHCs considerably less

amenable to catalysis and restricts access to stable modifications of this ligand class. In fact, the tendency of saturated NHCs towards dimerization is so pronounced that very few stable imidazolin-2-ylidenes are known in the literature.[2,3]

Herein, we describe the synthesis of a series of saturated NHCs that incorporate substituted naphthyl side chains. In order to extend the family of versatile NHC systems for catalysis, we reasoned that 2-substituted naphthyl side chains would be ideally suited for mimicking the successful architectures of the SIMes and SIPr ligand systems (Chart 1). Unexpectedly, the introduction of alkyl-substituents on the naphthyl moieties generates atropisomeric ligands with C_2-symmetric *(rac)* and C_s-symmetric (*meso*) conformations and we present an in depth study on the interconversion of these conformers. Whereas the parent naphthyl-substituted NHC ligand proved to be unstable as a free carbene, dimerizing rapidly to form the enetetramine, free carbenes of the other structures were generated in high yield and were characterized by X-ray crystallography.

To test the potential and versatility of our imidazolin-2-ylidenes in catalysis, we selected applications that include Palladium and Ruthenium catalyzed reactions and an example pertinent to their use in organocatalysis. Throughout, the new ligand systems show excellent catalytic activities and in a number of cases studied, they outperform the existing systems.



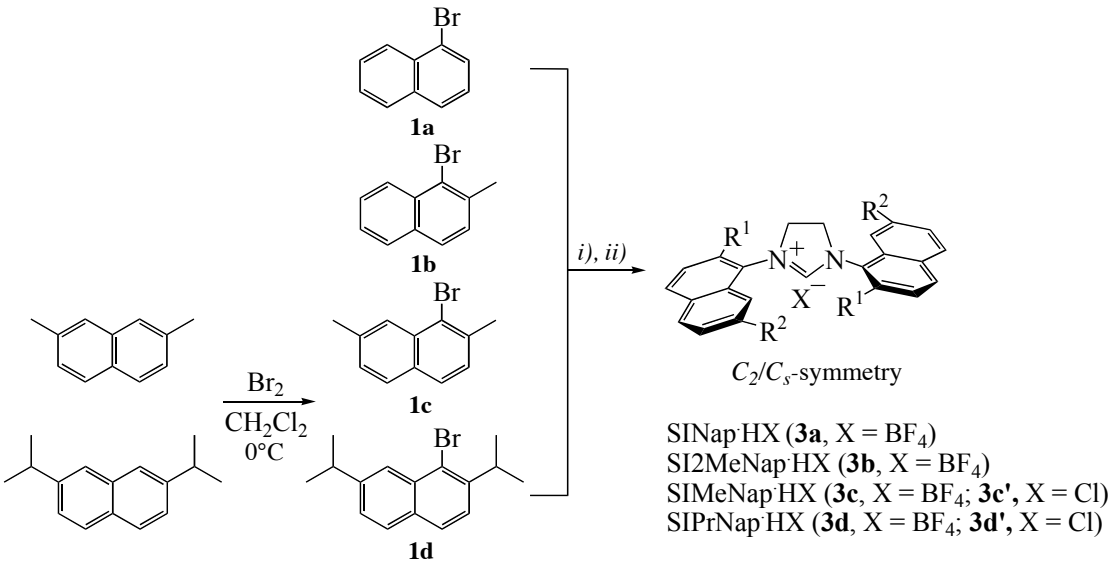
(1)

Chart 1. Imidazolin-2-ylidenes with phenyl (left) and naphthyl (right) side chains.

2.3 Results and Discussion

2.3.1 Synthesis and Characterization of Naphthyl-based Ligands: The synthesis of the imidazolinium salts **3a-3d** is summarized in Scheme 1. For both 2,7-dimethyl- and 2,7-isopropylnaphthalene, we first devised a bromination protocol to obtain **1c** and **1d**. Bromination in dichloromethane with slight cooling and without

addition of any catalyst/initiator provided the best results. Under these optimized reaction conditions, the initial bromination of the naphthyl derivatives turned out to be extremely selective and after workup, **1c** and **1d** were obtained in quantitative yield. Taking **1a-d**,[4] and following known synthetic procedures,[5] gave the saturated NHC salts **3a-3d** in good overall yield and high purity. Elucidation of SINap·HBF_4 [**3a**; 1,3-Bis(naphthalen-1-yl)-imidazolin-2-ylidene], SI2MeNap·HBF_4 [**3b**; 1,3-Bis(2-methylnaphthalen-1-yl)-imidazolin-2-ylidene], SIMeNap·HX [**3c** (X = BF_4)/**3c′** (X = Cl); 1,3-Bis(2,7-dimethylnaphthalen-1-yl)-imidazolin-2-ylidene; **3c**] and SIPrNap·HX [**3d** (X = BF_4)/**3d′** (X = Cl); 1,3-Bis(2,7-diisopropylnaphthalen-1-yl)-imidazolin-2-ylidene] by ^{1}H and ^{13}C NMR spectroscopy showed that SINap·HBF_4 (**3a**) adopts one conformation, while **3b**-**3d** and **3c′**/**3d′** gave rise to both *meso* (C_s-symmetric) and *racemic* (C_2-symmetric) isomers at room temperature (see discussion below for details). Full characterization of these new imidazolinium salts includes single crystal X-ray diffraction studies for **3b** and **3d′**. In both cases, the crystals measured correspond to the C_s-symmetric (*meso*) species and thermal ellipsoid drawings of the molecules can be found in Figure 1.



Scheme 1. Synthesis of imidazolinium salts. Reaction conditions; *i*) ethylenediamine, $Pd_2(dba)_3$/2(±)-BINAP (cat.), NaO^tBu, Toluene, 100°C; *ii*) Method A: NH_4BF_4, HCO_2H (cat.), $HC(OEt)_3$; Method B: HCl, THF; then $HC(OEt)_3$, MW.

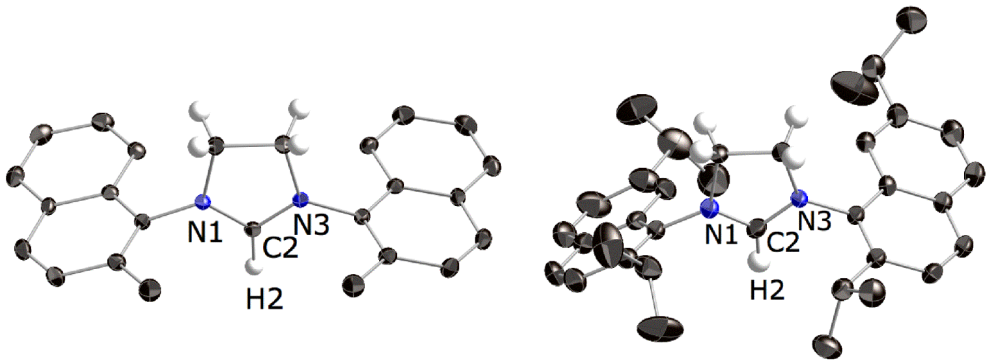
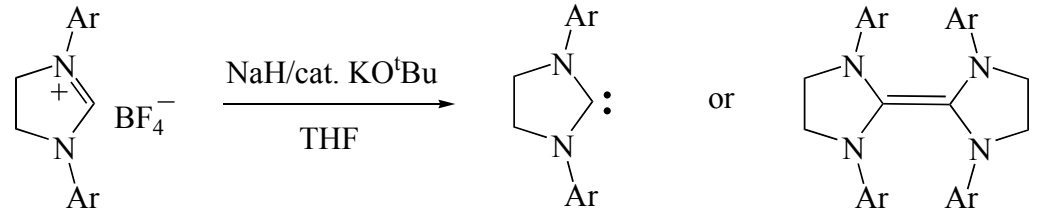


Figure 1. Thermal ellipsoid drawings of imidazolinium salts **3b** (left) and **3d′** (right). The anions and the hydrogen atoms except for the backbone and imidazolinium protons are omitted for clarity.

Deprotonation of **3b**-**3d** with NaH and catalytic amounts of potassium tert-butoxide led to clean formation of the free, monomeric carbenes **4b**-**4d** in high yields (Scheme 2). However, attempts to deprotonate SINap·HBF_4 (**3a**) (or SINap·HCl,[6]) with NaH/KO^{t}Bu, KH/DMSO or KHMDS invariably led to immediate formation of a bright orange solution containing the dimer SINap=SINap (**4a**) as the sole observable product.[7] To test the purely qualitative observation that the instability of **4a** might be due to the lack of the second ortho-substituent found in **4b**-**4d** (the first one being represented by the fused aromatic ring), we synthesized and fully characterized SIAnt·HBF_4 (**3e**; 1,3-Bis(anthracen-9-yl)-imidazolinium tetrafluoroborate, see experimental section). Indeed, deprotonation of this species, with both ortho positions 'protected' by fused aromatic rings, leads to clean formation of monomeric SIAnt (**4e**).[8]

According to the ^{1}H NMR and ^{13}C NMR spectra, the deprotonated products **4a**-**4c** adopt one conformation at 300 K. In the case of dimer **4a**, this implies that only one of the possible regioisomers is formed. For monomers SI2MeNap (**4b**) and SIMeNap (**4c**), the results suggest that deprotonation of the imidazolinium salt leads to a situation where the naphthyl sidechains are able to freely rotate due to the removal of the NHC-H bond. Finally, examination of the free N-heterocyclic carbene SIPrNap (**4d**) by ^{1}H NMR and ^{13}C NMR spectroscopy at 300 K shows two sets of signals corresponding to the presence of two isomers in an approximately 5:6 ratio (see VT experiments below). Thus, removal of the hydrogen does not seem to alter

the initial *rac*/*meso* ratio and we can therefore assume that in this case, a high enough barrier to rotation between the C_2- and C_s-conformations is maintained and no interconversion occurs during deprotonation.



SINap·HBF_4 (**3a**)
SI2MeNap·HBF_4 (**3b**)
SIMeNap·HBF_4 (**3c**)
SIPrNap·HBF_4 (**3d**)
SIAnt·HBF_4 (**3e**)

SINap (transient)
SI2MeNap (**4b**)
SIMeNap (**4c**)
SIPrNap (**4d**)
SIAnt (**4e**)

SINap=SINap (**4a**)

Scheme 2. Deprotonation of imidazolinium salts **3a-e**.

The identities of carbene dimer **4a** and of the free N-heterocyclic carbenes **4c** and **4d** were unambiguously established by single-crystal X-ray crystallography (Figure 2). Crystals of **4a** were obtained by slow evaporation of a saturated THF/Et_2O solution. The solid state structure of **4a** shows a strongly distorted carbene dimer, consistent with the structure of N,N',N'',N'''-tetraphenyl-bis(1,3-imidazolidin-2-ylidene).[9] The side view of the molecule reveals a small tetrahedral distortion at the nitrogen positions and non-planar 5-membered N-heterocycles. Similar distortions in related enetetramines have been documented in the literature and render the nitrogen atoms reactive and accessible, for example, to ready protonation of this type of molecule.[10] Crystals of **4c** suitable for X-ray analysis were obtained by slow evaporation of a saturated Et_2O solution, and crystals of **4d** were grown from saturated pentane/Et_2O solutions. In the solid state, SIMeNap (**4c**) shows its *meso* form, while the measured SIPrNap (**4d**) crystal corresponds to the racemic C_2-symmetric conformer. A comparison of bond lengths and angles with the only two other crystallographically characterized saturated NHCs, namely Arduengo's SIMes,[2a] and Denk's SI^{t}Bu,[3a] reveals a similar bonding situation for **4c** and **4d**. The N(1)–C(2)–N(3) angles [104.8(2)°; **4c** and 104.5(2)°; **4d**] are identical to SIMes [104.7(3)°], but slightly smaller than in SI^{t}Bu [106.44(9)°]. A clear difference can be seen in the planarity of the N-heterocycle. Whereas the backbone carbon atoms in

SIMes and SI^{t}Bu deviate measurably from the plane of the other three ring atoms, the N-heterocycles in **4c** and **4d** are almost perfectly planar.

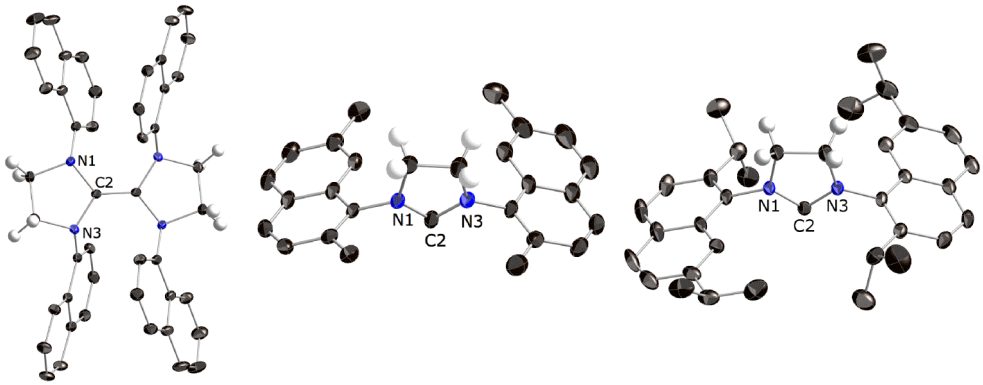


Figure 2. Thermal ellipsoid views of the SINap=SINap (**4a**, left), *meso*-SIMeNap (**4c**, middle) and *rac*-SIPrNap (**4d**, right). Hydrogen atoms on the side chains are omitted for clarity.

2.3.2 Variable-Temperature ^{1}H NMR Studies: VT ^{1}H NMR studies were performed in order to obtain more information on the dynamic behavior of the imidazolinium salts and the free imidazolin-2-ylidenes. Figure 3 schematically represents the rotation about the C–N bonds and color codes show the hydrogen atoms likely to be affected by the rotation.

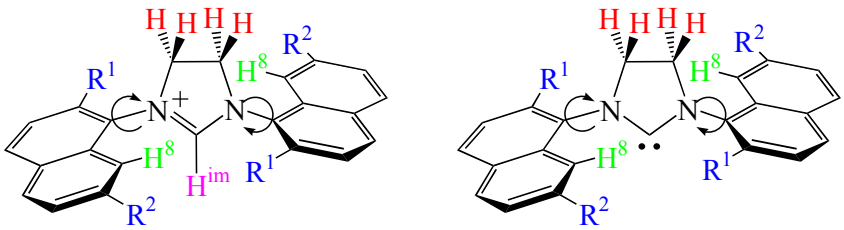


Figure 3. Schematic representation of the interconversion between the atropisomers.

Imidazolinium salts: VT ^{1}H NMR spectra of SINap·HBF$_4$ (**3a**) were measured in acetone-d_6 in the temperature range of 183-303 K. Only one set of signals was observed for the whole temperature range, meaning that the naphthyl substituents are rotating freely even at low temperature (183 K).

VT ^{1}H NMR spectra of SI2MeNap·HBF$_4$ (**3b**) show coalescence of the carbenic proton signals [δ 8.17 (H^{im}-C_2) and 8.36 (H^{im}-C_s) ppm] at 370 K (DMSO-

d_6), and above 380 K the protons of H^8 (green) and the NHC backbone protons (red) appear as broad singlets, indicating fast interconversion.

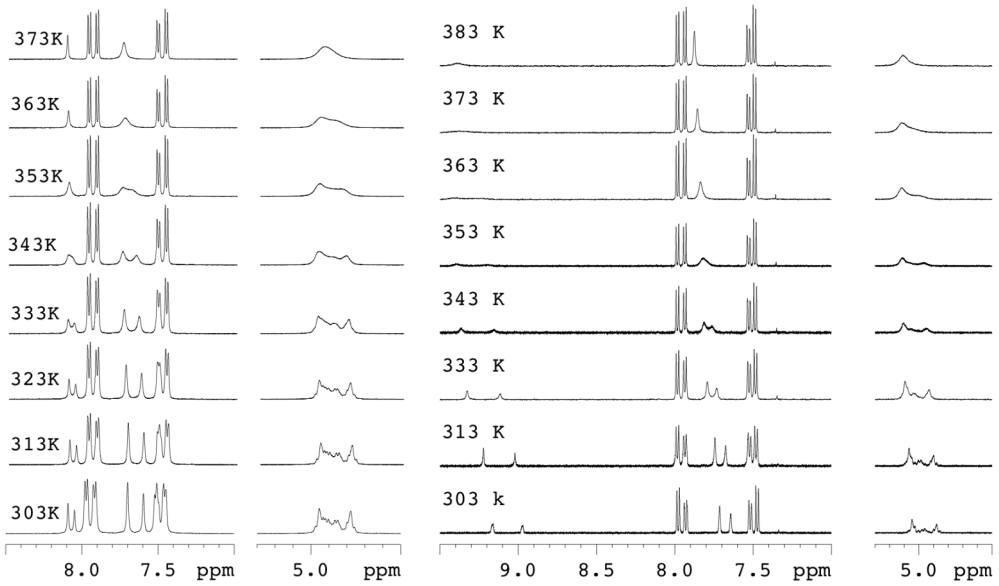


Figure 4. VT ^{1}H NMR spectra (500 MHz) of SIMeNap·HBF_4 (**3c**, left) and SIMeNap·HCl (**3c′**, right) in $C_2D_2Cl_4$.

VT ^{1}H NMR studies with different solvents (DMSO-d_6 and $C_2D_2Cl_4$) have been carried out for SIMeNap·HBF_4 (**3c**) and its chloride analogue, SIMeNap·HCl (**3c′**). In this case, the ^{1}H NMR spectrum of the imidazolinium chloride salt **3c′** is identical to that of its corresponding tetrafluoroborate salt **3c** in DMSO-d_6. However, significant differences between the spectra of **3c** and **3c′** in $C_2D_2Cl_4$ at 303K were observed (Figure 4). The signals of the imidazolinium proton in **3c′** shift to significantly lower magnetic field (ca. 1.0 ppm) with respect to the value for **3c**, presumably reflecting an increased contribution of hydrogen bonding between the H^{im}-proton and the chloride anion. When raising the temperature to the coalescence temperature, we find that both the nature of the counteranion (BF_4^- resp. Cl^-) as well as the choice of the solvent (DMSO-d_6 or $C_2D_2Cl_4$) do not affect the ease of interconversion for **3c** and **3c′**. Furthermore, the process is almost not affected by the introduction of the 7-methyl group and coalescence temperatures for SI2MeNap·HBF_4 (**3b**) and SIMeNap·HBF_4 (**3c**) are practically identical.

The VT ^{1}H NMR spectra in DMSO-d_6 of **3d** and **3d′** showed a static behavior, with no detectable line-shape modifications up to 420 K. Undoubtedly, the decrease

in fluxional behavior is caused by the increased size of the ortho-substituents on the naphthyl moieties (isopropyl *vs* methyl).

Free NHCs: VT ^{1}H NMR experiments were also performed on solutions of **4b**-**4d**. In the case of **4b** and **4c**, interconversion of the two atropisomeric conformations at room temperature leads to the observation of a single signal for the H^8 protons (δ = 8.18 ppm for **4b** and δ = 8.02 ppm for **4c** in toluene-d_8). Lowering the temperature showed gradual broadening of these signals with decoalescene at 273 K (**4b**) and 293 K (**4c**). The formation of two sets of ^{1}H NMR signals in the slow-exchange regime is again consistent with the dynamic interconversion between *meso*- and *rac*-conformers. With SIPrNap (**4d**), two sets of signals were observed at room temperature and fully attributed to the *rac* and *meso* forms. By raising the temperature, coalescence of the resonance signals at δ 8.00 and 8.10 ppm (H^8 proton) was achieved at 350 K, and above 360 K the signal appeared as a sharp singlet at δ 8.02 ppm (Figure 5).

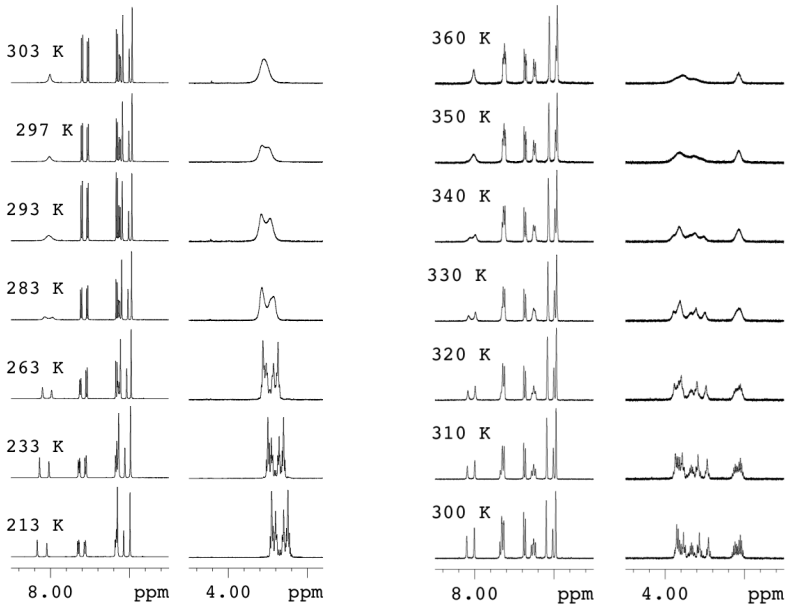


Figure 5. VT ^{1}H NMR spectra (400 MHz) of free carbenes **4c** (left) and **4d** (right) in toluene-d_8.

Activation free Energies: From the VT analyses performed above, we calculated activation free energies $\Delta G^{\ddagger}$ at the coalescence temperature (T_c) for the interconversion, using complete line-shape analysis,[11] which gave the corresponding $\Delta G^{\ddagger}$ (kJ mol^{-1}) values (Table 1). It is evident from the data that the rotational barriers decrease in the order (**3d** = **3d′**) > (**3c** = **3c′**) ≈ **3b** > **3a** for the salts, and **4d** > **4c** > **4b**

for the free NHCs. These trends can be clearly associated with the steric demand of the naphthyl side chains. More specifically, substituents at both the 2- and 7-positions of the naphthyl moieties affect $\Delta G^{\ddagger}$, with the 2-position playing a crucial factor limiting the rotation about the C–N bond between the side chains and the five-membered central ring. Moreover, $\Delta G^{\ddagger}$ decreases by about 20 kJ mol^{-1} when removing the carbenic proton, that is when going from the imidazolinium salts to the free carbenes.

Table 1. Values of T_c, the corresponding $\Delta G^{\ddagger}$'s and DFT values for $\Delta G^{\ddagger}$.

Entry	Compound	Solvent	T_c (K)	$\Delta G^{\ddagger}$ (kJ mol^{-1})	DFT $\Delta G^{\ddagger}$ (kJ mol^{-1})
1	**3a**	acetone-d_6	< 183	<44.1	30
2	**3b**	DMSO-d_6	370 (H^8)	74.6	75
3	**3c**	$C_2D_2Cl_4$	353 (H^{im})	75.5	74
4	**3c′**	$C_2D_2Cl_4$	373 (H^{im})	75.5	-
5	**3c** or **3c′**	DMSO-d_6	350 (H^{im})	75.6	-
6	**3d** or **3d′**	DMSO-d_6	> 410	>89.9	80
7	**4b**	toluene-d_8	273 (H^8)	56.9	54
8	**4c**	toluene-d_8	293 (H^8)	59.8	54
9	**4d**	toluene-d_8	350 (H^8)	74.4	70

2.3.3 Calculations on the Chemical/Conformational Stability and Steric Characterization of the Ligands: DFT calculations in the solvent phase confirm that the *rac* and *meso* isomers of **4b-d** are of substantially the same energy (within 3 kJ mol^{-1}), and this difference is scarcely dependent on the solvent, since calculations in THF or toluene resulted in very similar values (within 1-2 kJ mol^{-1}). In excellent agreement with the experimental $\Delta G^{\ddagger}$'s, the DFT barrier in toluene for the interconversion of the *rac* isomer into the *meso* isomer is quite similar in **4b** and **4c** (around 54 kJ mol^{-1}), and increases to 70 kJ mol^{-1} in **4d**. Rotation in the monomeric species SINap, instead, presents the negligible barrier of 3 kJ mol^{-1}. With regards to the dimerization of the free NHCs to the corresponding enetetramines, we calculated that dimerization of SINap in THF is favored by 15 kJ mol^{-1}, whereas **4b-d** were calculated to be thermodynamically stable as monomers. However, while **4b** and **4c** are slightly more stable than the dimer (by 10 and 29 kJ mol^{-1}, respectively), dimerization of **4d** is remarkably unfavored (by 106 kJ mol^{-1}). Similar excellent agreement between the DFT and the experimental values is obtained for the rotational

barriers in the **3a-3d** salts. In all cases, the salts present a barrier to rotation roughly 20 kJ mol^{-1} higher than in the corresponding free NHC.

These results clearly support the idea that the behavior of SINap and **4b-4d** is determined by the nature of the group in position 2 of the binaphthyl framework. With a hydrogen atom in this position, such as in SINap, rotation around the N–naphthyl bond is completely free, and dimerization to the enetetramine SINap=SINap (**4a**) is favored. With a methyl group in this position, such as in **4b** and **4c**, rotation around the N–naphthyl bond presents a moderate barrier, and dimerization is moderately disfavored. Finally, with a bulky isopropyl group in this position, such as in **4d**, rotation around the N–Ar bond is frozen at room temperature, and dimerization is clearly unfavored.

Table 2. Steric parameter $\%V_{Bur}$ corresponding to SINap and **4b-4d**.

Entry	NHC	$\%V_{Bur}$	
		rac-isomer	*meso*-isomer
1	SINap	26	26
2	SI2MeNap (**4b**)	28	27
3	SIMeNap (**4c**)	29	28
4	SIPrNap (**4d**)	31	31
5	IMes	26[a]	
6	SIMes	27[a]	
7	IPr	29[a]	
8	SIPr	30[a]	

[a] Values taken from ref. 13.

To further characterize this new ligand family, we calculated the percent of buried volume $\%V_{Bur}$, a molecular descriptor that can be considered as an analogue of Tolman's cone angle for tertiary phosphines,[12] and that can be successfully used to classify the steric properties of NHC ligands.[13,14] Table 2 shows that the $\%V_{Bur}$ of SINap is smaller than the value previously calculated for SIMes ($\%V_{Bur}$ = 27), while $\%V_{Bur}$ of **4b** and **4c** indicate a slightly bulkier nature than their mesityl-substituted counterparts. It is of interest to note that the $\%V_{Bur}$ of the *meso* isomer is usually smaller than that of the *rac* isomer. Finally, the $\%V_{Bur}$ of SIPrNap (**4d**) is somewhat larger than the $\%V_{Bur}$ of the SIPr ligand ($\%V_{Bur}$ = 30). In short, this analysis confirms the starting hypothesis that **4b** and **4c** should substantially mimick the IMes/SIMes ligands, while the steric requirements of **4d** are best compared to the SIPr ligand.

2.3.4 Catalytic Applications: Palladium Catalysis. Pioneering work by Nolan et al. has shown that NHC–modified Pd–allyl catalysts are extremely active systems in various cross-coupling reaction protocols.[15] By following their experimental procedure, addition of $[Pd(allyl)Cl]_2$ to free carbenes **4b-d** gave high yields of *rac*/*meso* mixtures of our compounds with general formula (NHC)Pd(allyl)Cl (**5b-d**). Attempts to separate these *rac/meso* mixtures via column chromatography using a variety of different eluents were unsuccessful and the compound mixtures were recovered unchanged. In contrast, repeated crystallization from CH_2Cl_2/hexane and ethyl acetate/hexane (see Experimental Section) enabled the separation of both **5c** and **5d** into *meso*-**5c**, *rac*-**5c**, and *meso*-**5d**, *rac*-**5d** respectively. NMR analyses gave distinct signals for the *rac* and *meso* complexes and to assign their conformation unambiguously, the crystal structures of all four compounds were determined (Figure 6). As could be anticipated from the studies on our NHC salts, the formation of the NHC–metal bond efficiently freezes the rotation around the C–N bonds of the NHC side chains.

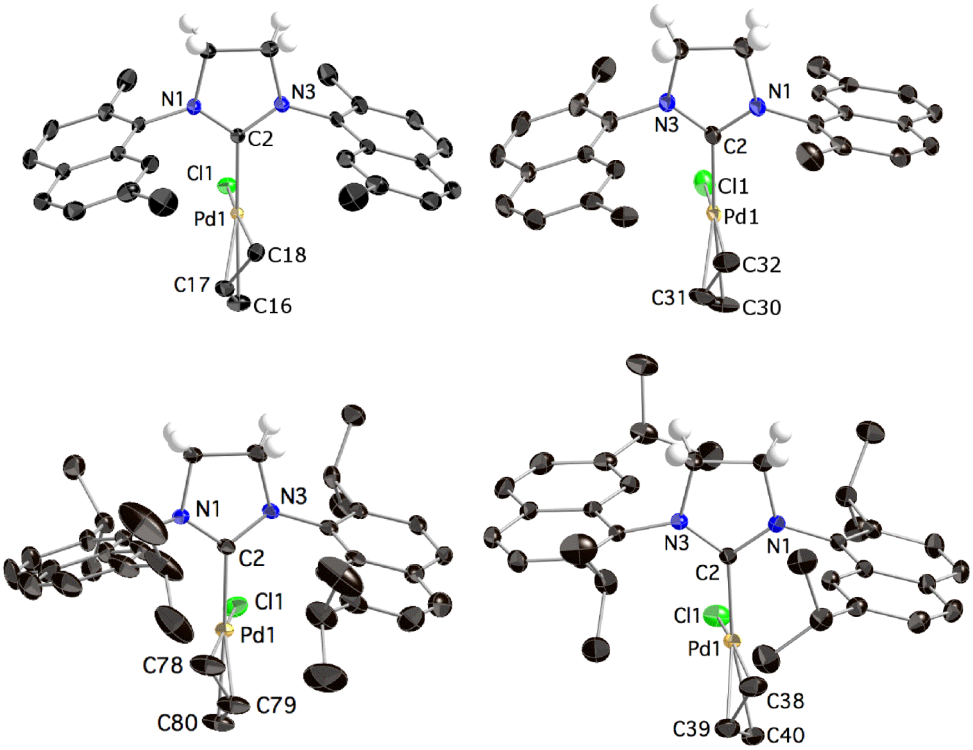
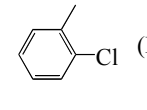
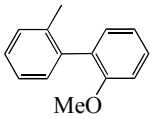
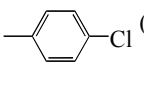
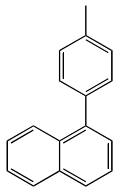
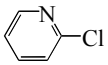
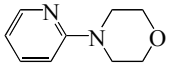
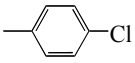
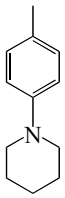


Figure 6. Crystal structures of (*meso*-SIMeNap)Pd(allyl)Cl (*meso*-**5c**, top left), *rac*-SIMeNapPd(allyl)Cl (*rac*-**5c**, top right), (*meso*-SIPrNap)Pd(allyl)Cl (*meso*-**5d**, bottom left), and *rac*-SIPrNapPd(allyl)Cl (*rac*-**5d**, bottom right).

Considering the excellent performance of DFT in reproducing the experimental rotational barrier between the *rac* and *meso* isomers in the free NHCs, we used the same approach to predict the *rac* to *meso* rotational barrier in the catalytically active compounds, presumed to have the formula (NHC)Pd(0). Even for the less encumbered (SI2MeNap)Pd(0) and (SIMeNap)Pd(0) intermediates we found a high barrier for rotation (102 and 103 kJ mol^{-1} in toluene), which suggests that the respective symmetry of the ligands (*rac* or *meso*) should be retained during catalysis.

Initial catalytic studies with our palladium complexes indicated that the reactivity of *meso*-**5c** (*meso*-**5d**) is essentially the same as the reactivity seen for *rac*-**5c** (*rac*-**5d**) (see Supporting Information). For convenience, all of the following catalytic applications were therefore run with *rac*/*meso* mixtures of the precatalysts. Rather bulky substrates were chosen in the Suzuki-Miyaura cross-coupling reactions of aryl chlorides (Table 3, entries 1-20). Especially when both coupling partners are ortho-substituted (entries 1-10), our naphthyl-based catalysts perform better than the corresponding (SIMes)Pd(allyl)Cl [**SIMes-Nolan**] and (SIPr)Pd(allyl)Cl [**SIPr-Nolan**] systems and display high activity at 80°C.[16] Significant reactivity differences between **5b-5d** can only be seen when the reactions are run at room temperature, where SIPrNap-modified **5d** gives better conversions than the catalysts derived from methyl-substituted **5b** and **5c**. In contrast, activity differences are dramatic in the Hartwig-Buchwald amination with difficult aryl-chloride substrates (entries 21-31), where we see an enormous drop in catalyst performance when moving from the SIPr/SIPrNap systems (excellent reactivity) to SIMes-, SI2MeNap- and SIMeNap-modified palladium complexes, which are rather poor catalysts for the substrates studied. In these amination protocols, small changes in the sterics of the NHC ligand system seem to have a big impact on the activity of the catalysts and the bulkiest systems (**SIPr-Nolan** and **5d**) become the catalysts of choice for these transformations.

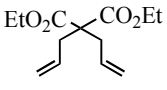
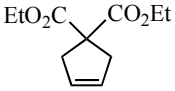
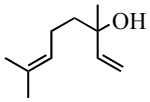
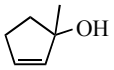
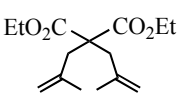
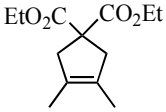
Table 3. Selected Pd-catalyzed C-C and C-N couplings with **5b-d**.

Entry	Ar-Cl	Amine or B-acid	Product [c]	Catalyst (1 mol%)	Time	Temp.	Yield[a]
1				**SIMes-Nolan**	1h	80°C	<5%
2				**5b**	1h	80°C	98%
3				**5c**	1h	80°C	98%
4				**SIPr-Nolan**	1h	80°C	59%
5				**5d**	1h	80°C	99%
6				**SIMes-Nolan**	16h	RT	<5%
7				**5b**	16h	RT	43%
8				**5c**	16h	RT	58%
9				**SIPr-Nolan**	16h	RT	57%
10				**5d**	16h	RT	75%
11				**SIMes-Nolan**	1h	80°C	82%
12				**5b**	1h	80°C	95%
13				**5c**	1h	80°C	97%
14				**SIPr-Nolan**	15min	80°C	86%
15				**5d**	15min	80°C	99%
16				**SIMes-Nolan**	16h	RT	79%
17				**5b**	16h	RT	75%
18				**5c**	16h	RT	81%
19				**SIPr-Nolan**	3h	RT	83%
20				**5d**	3h	RT	98%
21				**SIMes-Nolan**	24h	RT	88%
22				**5b**	24h	RT	95%
23				**5c**	96h	RT	89%
24				**SIPr-Nolan**	1min	RT	99%
25				**5d**	1min	RT	99%
26				**5d** (0.1 mol%)	6h	RT	95%
27				**SIMes-Nolan**	20h	80°C	11%
28				**5b**	20h	80°C	23%
29				**5c**	20h	80°C	4%
30				**SIPr-Nolan**	10min	80°C	99%
31				**5d**	10min	80°C	99%

[a] Yields determined by GC against internal standard. Reaction times and conditions of the reference systems (SIMes)Pd(allyl)Cl [**SIMes-Nolan**] and (SIPr)Pd(allyl)Cl [**SIPr-Nolan**] were chosen according to the results for **5b**/**5c** and **5d** respectively.

2.3.5 Ruthenium Catalysis. One of the most important applications of NHCs in metal catalysis is undoubtedly their use as ligands in Ru-catalyzed metathesis reactions.[17] The general interest in these transformations compelled us to examine analogues of Grubbs' second generation catalyst [$RuCl_2$(SIMes)(=CHPh)(PCy_3)],[17c] incorporating ligand systems **4b-d**. Synthesis was achieved by simple exchange of one phosphine ligand with NHCs **4b-d** in toluene.[17b] Appropriate workup gave [$RuCl_2$(SI2MeNap)(=CHPh)(PCy_3)] (**6b**), [$RuCl_2$(SIMeNap)(=CHPh)(PCy_3)] (**6c**) and [$RuCl_2$(SIPrNap)(=CHPh)(PCy_3)] (**6d**) in good yields. We then employed catalysts **6b**-**6d** in the ring-closing metathesis of three standard substrates (Table 4, entries 1-14). Except for a slightly lower reaction temperature (27°C instead of 30°C), standard reaction conditions were used,[18] and the conversions were monitored by ^{1}H NMR spectroscopy. While the reactivities of **6b** and **6c** closely resemble that seen with SIMes-modified Grubbs II, catalyst **6d** gave markedly superior results. In fact, **6d** outperforms Grubbs II by an order of magnitude and RCM of all three substrates runs to completion in less than one hour with only 0.1 mol% of **6d**, corresponding to turnover frequencies for complete conversion at 27°C of up to 2'400 TOF (entry 10). Even trisubstituted diolefin linalool reacts readily under these conditions, at the same time showing a pronounced induction period that is absent for the other two substrates or at 1 mol% catalyst loading (Figure 7). Interestingly, the introduction of alkylated naphthyl side chains renders catalysts **6b-d** more active towards RCM of diethyldimethallyl malonate (entries 15-18).[19] In recent years, enhancement of reactivities by fine-tuning [$RuCl_2$(SIMes)(=CHPh)(PCy_3)] (Grubbs II) have been observed and have by and large been achieved by modifying every other entity of the precatalyst.[20,21,22,23] Unfortunately, such approaches often involve additional synthetic steps and are normally exclusive and limited to ruthenium metathesis. On the other hand, successful modifications to the NHC structure as presented here with SIPrNap may prove valuable in a plethora of other catalytic applications and certainly highlight the pivotal role played by the NHC ligand architecture in these systems.[24]

Table 4. RCM of standard dienes employing catalysts **6b-d**.

Entry	Diene	Product	Catalyst	Loading (mol%)	Temp.	t (min)	Conv.[a]
1			**Grubbs II**	1	30°C	42	98%[b]
2			**6b**	1	27°C	70	98%
3			**6c**	1	27°C	65	98%
4			**6d**	1	27°C	17	98%
5			**6d**	0.1	27°C	52	98%
6			**Grubbs II**	1	25°C	90	98%[c]
7			**6b**	1	27°C	54	98%
8			**6c**	1	27°C	28	98%
9			**6d**	1	27°C	10	100%
10			**6d**	0.1	27°C	25	100%
11			**6b**	1	27°C	18	100%
12			**6c**	1	27°C	19	100%
13			**6d**	1	27°C	7	100%
14			**6d**	0.1	27°C	35	100%
15			**Grubbs II**	5	30°C	96 h	17%[b]
16			**6b**	5	27°C	72 h	30%
17			**6c**	5	27°C	72 h	40%
18			**6d**	5	27°C	72 h	31%

[a] Conversions determined by ^{1}H NMR spectroscopy. For better comparison, a fixed conversion of 98% was used for entries 1-8. [b] Taken from ref. 18. [c] Taken from ref. 21a.

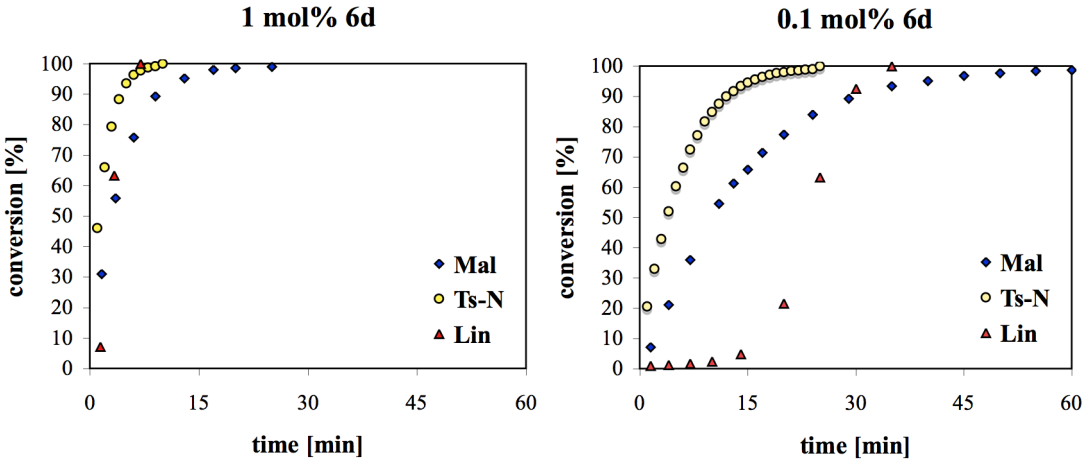
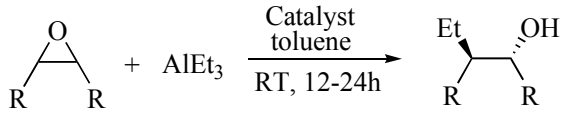


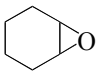
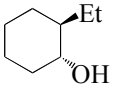
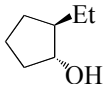
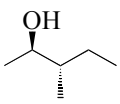
Figure 7. Conversion to product at 27°C with 1 mol% (left) and 0.1 mol% (right) of catalyst **6d**. Abbreviations used: Mal (Diethyldiallyl malonate), Ts-N (N,N-Diallyl-4-methyl-benzenesulfonamide), and Lin (Linalool).

2.3.6 Alkylation of Epoxides. With the excellent catalytic results obtained above in both palladium and ruthenium mediated reactions, we finally wanted to see whether our systems could also be used as catalytic Lewis bases for the ring-opening alkylation of epoxides by alkylaluminum reagents. Initial studies by Schneider et al.

on the use of phosphine and arsine bases in these transformations,[25] have more recently been followed by Nguyen's finding that bulky NHC salts could also be employed.[26] The best NHC-derived catalyst turned out to be a substructure of SIPr·HBF_4 with two additional methyl groups on the backbone of the N-heterocycle (for simplicity, we call this ligand DMSIPr·HBF_4), whereas Schneider et al. have identified $AsPh_3$ as the best base in their studies. The reactivity of SI2MeNap·HBF_4 (**3b**), SIMeNap·HBF_4 (**3c**) SIPrNap·HBF_4 (**3d**) is superior to the benchmark catalysts reported in the literature (Table 5). In fact, catalytic ring-opening of cyclohexene oxide could be easily run with only 1 mol% of catalyst (versus 5 mol% for the reference systems) and resulted in products of equal or higher yields (entries 1-6). Even better results were obtained with more challenging substrates cyclopentene oxide and 2,3-butene oxide (entries 7-16). Furthermore, build-up of side products as observed by Nguyen et al. with SIPr·HBF_4 and DMSIPr·HBF_4 was not observed with our catalysts. Within our ligand family, we again identify SIPrNap·HBF_4 (**3d**) as the most competent substructure, giving almost quantitative yields with all products.

Table 5. NHC-catalyzed ring-opening alkylation of epoxides.



Entry	Epoxide	Product	Catalyst	Loading (mol%)	t (h)	Yield[a]
1			$AsPh_3$	5	24	94%[b]
2			SIPr·HBF_4	5	12	71%[c]
3			DMSIPr·HBF_4	5	12	93%[c]
4			**3b**	1	12	98%
5			**3c**	1	12	95%
6			**3d**	1	12	93%
7			$AsPh_3$	5	24	75%[b],[d]
8			DMSIPr·HBF_4	5	12	77%[c]
9			**3b**	1	24	90%
10			**3c**	1	24	91%
11			**3d**	1	24	97%
12			$AsPh_3$	5	24	62%[b]
13			DMSIPr·HBF_4	5	12	53%[c]
14			**3b**	1	20	61%
15			**3c**	1	20	78%
16			**3d**	1	20	96%

[a] Yields after workup, determined by GC against internal standard. [b] Taken from ref. 25. [c] Taken from ref. 26. [d] Reaction conducted at 50°C.

2.4 Conclusions

We have presented a new class of saturated NHC ligands with naphthyl-derived side chains. An initial, highly selective bromination protocol was devised for some of the substituted naphthyl moieties and renders the synthetic pathway to all of the imidazolinium salts easy and straightforward. Deprotonation of the salts yielded a dimer in the case of SINap, whereas with substituted naphthyl as well as with anthracenyl side chains, high yields of the free carbenes and rare examples of crystallographically characterized imidazolin-2-ylidenes were obtained. The stability of the monomers is explained by using computational methods. In both the NHC salts and the free carbenes, introduction of substituted naphthyl side chains gives rise to C_2-symmetric *(rac)* and C_s-symmetric (*meso*) atropisomers. In depth experimental and computational analyses for the interconversion between the two isomers showed that as soon as the NHC carbon atom is bound to either a hydrogen (for the NHC salt) or a metal (NHC-Pd), the rotation around the C-N bonds becomes highly unfavorable.

At the outset of the present study, we sought the identification of viable N-heterocyclic carbene alternatives to the widely used and versatile IMes/SIMes and IPr/SIPr architectures. The preliminary catalytic results presented here exceeded our expectations. Not only were we able to demonstrate that this new naphthyl-based NHC ligand family presents similar versatility to the reference systems and can (at least) be employed in palladium-based coupling reactions, in ruthenium-based metathesis and in the organocatalytic ring-opening alkylation of epoxide, but more importantly, we were able to show that catalytic activities were at least as high or higher than in the reference systems. In the palladium-catalyzed reactions, generally better reactivities than with the corresponding SIMes- and SIPr-modified Nolan catalysts were obtained, with SIPrNap outperforming the methyl-substituted ligands. Better still, the naphthyl-substituted NHCs described here are the catalysts of choice for the organocatalytic ring-opening alkylation of epoxides, giving higher yields of products at lower catalyst loadings than the reference systems described in the literature. Of possibly even greater significance is the identification of precatalyst $[RuCl_2(SIPrNap)(=CHPh)(PCy_3)]$ (**6d**) as a rapidly initiating species in metathesis. In fact, the preliminary results here show that **6d** outperforms Grubbs II in the ring-

closing metathesis by an order of magnitude, making it a very appealing alternative to existing catalyst systems.

One of our long-term goals is the identification of a family of broadly applicable chiral NHC ligands and we believe that the unique architecture of the naphthyl-based N-heterocyclic carbenes we describe here presents an ideal starting point for such a study.

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Supporting Information Available: Experimental procedures for the ligands, spectroscopic data, computational methods and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

2.5 Computational Part

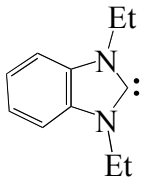
The density functional calculations were performed on all the systems at the GGA level with the Gaussian03 set of programs.[27] For the BP86 calculations, gradient corrections were taken from the work of Becke and Perdew.[28] The electronic configuration of the molecular systems was described by the triple-ζ basis set with polarization functions of Ahlrichs and co-workers (TZVP basis set in gaussian03).[29] Solvent effects including contributions of non electrostatic terms have been estimated in single point calculations on the gas-phase optimized structures, based on the polarizable continuous solvation model PCM, default keyword SCRF = (Solv = X) with X = THF, toluene, acetone or methanol, in gaussian03.[30] Transition states for the rac/meso isomerization were approached by rotating the R1 group around the N-R1 bond in 10° steps. Full transition state searches were started from the maximum of this curve, and frequency calculations were performed on the final geometries to confirm the presence of only one negative value. The free energy barrier in solution was obtained as the free energy in the gas-phase corrected by the free-energy of

solvation through single-point calculations with the PCM approach, on the rac isomer and on the transition state geometry.

The dimerization energies have been calculated as the energy difference between the optimized geometries of the dimer NHC=CHN and of two monomers NHC, as shown in eq. S1.

$$2\ \text{NHC:} \Leftrightarrow \text{NHC=CHN} + -E_{\text{dim}}. \qquad \text{(S1)}$$

Calculations have been performed with the gaussian03 package at the BP86 level of theory together with the TZVP basis set. Solvent effects were estimated through single-point calculations with the PCM approach on both the monomer and the dimer. To validate this approach we calculated the dimerization energy of the NHC **S1**, whose free energy of dimerization, about 5 kcal/mol in diglyme at 298 K, has been determined experimentally.[31]



S1

With our approach in THF, we calculate an E_{dim} = 7.3 kcal/mol for **S1**, which is rather close to the experimental value, and substantially validate our strategy for the calculation of the dimerization energy.

2.6 Experimental Part

General Information. All reactions were carried out under a nitrogen atmosphere using Standard Schlenk-lines or gloveboxes (Mecaplex or Innovative Technology). All reagents were used as received unless otherwise noted. Solvents were purchased in the best quality available, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Solvents for NMR spectroscopy were degassed with nitrogen and dried over molecular sieves. NMR spectra were recorded on AV2 400 or AV2 500 MHz Bruker spectrometers. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). High-resolution mass spectra (HRMS) were performed on a *Finnigan MAT 95* (*Finnigan MAT95*, San Jose, CA;

USA) double-focusing magnetic sector mass spectrometer (geometry BE). ESI mass spectra were performed on a triple stage quadrupole instrument (*Finnigan TSQ 700*, San Jose, CA; USA), equipped with a combined Finnigan Atmospheric Pressure Ion (API) source. GC-MS analysis was done on a Finnigan Voyager GC8000 Top. GC analyses of reaction mixtures were carried out on a Trace GC 2000 equipped with an FID detector. The column used was a 30-m ZB-5 capillary column with 0.25-mm inner diameter and 0.25-μm film thickness. Flow rate = 1.5 mL/min for He carrier gas. GC yields were determined through integration of the product peak against internal standard using pre-established response factors. Retention times for various components of the reaction mixture were assigned by injection of a pure sample of each component. X-ray crystallography was performed on a *Nonius Kappa CCD* area-detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. N,N-Diallyl-4-methylbenzenesulfonamide was prepared according to a literature procedure.[32]

N,N′-Bis(naphthalen-1-yl)ethane-1,2-diamine (2a). A 100 mL two necked flask was charged with $Pd_2(dba)_3$ (65 mg, 0.07 mmol), (±)-BINAP (88 mg, 0.14 mmol), NaO^tBu (410 mg, 4.26 mmol) and toluene (25 mL) in the glovebox. 1-bromonaphthalene (**1a**) (417 μL, 2.98 mmol) and ethylenediamine (95 μL, 1.42 mmol)) were added by syringe outside the glovebox. The reaction mixture was stirred at 100°C for 17 h under nitrogen. After cooling to room temperature, it was filtered through a silica gel filter, washed with 300 mL hexane and the product was collected by washing with 400 mL CH_2Cl_2. The CH_2Cl_2 fraction was dried by rotavapor to give 421 mg (95%) of **2a** as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.77 (m, 4H), 7.47-7.37 (m, 4H), 7.36 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.3 Hz, 2H), 6.74 (d, J = 7.8 Hz, 2H), 4.64 (br s, 2H), 3.72 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.87, 134.56, 128.90, 126.65, 126.13, 125.31, 124.02, 120.24, 118.83, 105.74, 43.93. HRMS (EI) m/z calculated for $C_{22}H_{20}N_2$ $[M]^+$ 312.1626, observed 312.1622.

1,3-Bis(naphthalen-1-yl)-imidazolinium tetrafluoroborate (SINap·HBF$_4$) (3a). Triethyl orthoformate (18 mL) was added to the diamine (**2a**) (470 mg, 1.50 mmol) in a 50 mL Schlenk flask equipped with a distillation head. To this solution were added NH_4BF_4 (157 mg, 1.50 mmol) and 2 drops of formic acid. The reaction was heated to 100 °C and stirred for 12 h. Upon cooling to room temperature, the white precipitate

was collected by filtration, washed with Et_2O and pentane and dried in vacuo to yield 449 mg (73%) of the title product. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.53 (s, 1H), 8.41 (d, J = 8.3 Hz, 2H), 8.18-8.13 (m, 4H), 7.98 (d, J = 7.0 Hz, 2H), 7.82-7.78 (m, 2H), 7.75-7.71 (m, 4H), 4.78 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 159.76, 133.92, 132.43, 130.15, 128.60, 128.14, 127.85, 127.27, 125.72, 124.62, 122.38, 53.65. ^{19}F NMR (DMSO-d_6, 376.4 MHz): -148.28, -148.33. HRMS (ESI) m/z calculated for $C_{23}H_{19}N_2$ $[M\text{-}BF_4]^+$ 323.1548, observed 323.1547.

2-(1,3-Di-1-naphthalenyl-2-imidazolidinylidene)-1,3-di-1-naphthalenyl-imidazolidine (4a). A suspension of NaH (26 mg, 1.10 mmol) and KO^{t}Bu (6 mg, 5.00×10^{-2} mmol) in 10 mL THF was added to a suspension of SINap·HBF_4 (**3a**) (410 mg, 1.00 mmol) in 10 mL THF. The reaction was stirred for 2 h at rt in the glovebox, filtered through celite and dried in vacuo to yield 200 mg (62%) of a red solid. Crystals suitable for an X-ray diffraction study were grown from a THF/Et_2O solution. ^{1}H NMR (THF-d_8, 400 MHz): δ 7.71-6.82 (m, 28H), 3.90 (br, 4H), 3.15 (br, 4H); ^{13}C NMR (THF-d_8, 100 MHz): δ 145.38, 135.43, 130.47, 127.88, 125.87, 125.26, 124.77, 124.64, 123.93, 120.35, 112.88, 55.20.

N,N′-Bis(2-methylnaphthalen-1-yl)ethane-1,2-diamine (2b). In the glovebox a 100 mL two necked flask was charged with $Pd_2(dba)_3$ (114 mg, 0.12 mmol), (±)-BINAP (156 mg, 0.25 mmol), NaO^{t}Bu (720 mg, 7.50 mmol), 1-bromo-2-methylnaphthalene (**1b**) (1.16 g, 5.25 mmol) and toluene (50 mL). Ethylenediamine (167 µL, 2.50 mmol) was added by syringe outside the glovebox. The reaction mixture was stirred at 100°C for 16 h under nitrogen. It was then plugged through a silica gel filter, washed with CH_2Cl_2, concentrated in vacuo, and the residue was purified by flash chromatography using CH_2Cl_2 as eluent to yield 760 mg (89%) of **2b** as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (d, J = 7.9 Hz, 2H), 7.81 (d, J = 7.9 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.49-7.40 (m, 4H), 7.31 (d, J = 8.4 Hz, 2H), 3.92 (br s, 2H), 3.48 (s, 4H), 2.49 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.02, 133.57, 129.41, 128.67, 128.39, 125.85, 125.57, 124.93, 122.92, 122.57, 50.51, 18.29. HRMS (EI) m/z calculated for $C_{24}H_{24}N_2$ $[M]^+$ 340.1939, observed 340.1943.

1,3-Bis(2-methylnaphthalen-1-yl)-imidazolinium tetrafluoroborate [SI2MeNap·HBF_4] (3b). Triethyl orthoformate (25 mL) was added to the diamine (**2b**) (760 mg, 2.23 mmol) in a 50 mL schlenk flask equipped with a distillation head. To this solution were added NH_4BF_4 (234 mg, 2.23 mmol) and 2 drops of formic acid.

The reaction was heated to 100 °C and stirred for 12 h. Upon cooling to room temperature, the white precipitate was collected by filtration, washed copious amounts of Et_2O and dried in vacuo to yield 858 mg (88%) of the title product. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.47 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.2 Hz, 1H), 8.12-8.08 (m, 4H), 7.86-7.77 (m, 2H), 7.70-7.61 (m, 4H), 4.90-4.65 (m, 4H), 2.70 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz) (due to the existence of two atropisomers, the ^{13}C NMR spectrum is complex): δ 164.38, 161.72, 161.60, 134.20, 134.08, 132.47, 130.28, 130.27, 129.28, 129.27, 129.24, 129.15, 128.97, 128.93, 128.54, 128.44, 128.30, 128.25, 126.46,121.89, 121.45, 52.44, 52.41, 17.68, 17.59. ^{19}F NMR ($CDCl_3$ 282.4 MHz): -154.03, -154.08. HRMS (ESI) m/z calculated for $C_{25}H_{23}N_2$ $[M\text{-}BF_4]^+$ 351.1861, observed 351.1864.

1,3-Bis(2-methylnaphthalen-1-yl)-imidazolin-2-ylidene [SI2MeNap] (4b). A suspension of NaH (26 mg, 1.10 mmol) and KO^{t}Bu (6 mg, 5.00×10^{-2} mmol) in 10 mL THF was added to a suspension of SI2MeNap·HBF_4 (**3b**) (438 mg, 1.00 mmol) in 10 mL THF. The reaction was stirred overnight at rt in the glovebox, filtered through celite and dried in vacuo to yield 338 mg (96%) of the white free carbene. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.27 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.47-7.41 (m, 2H), 7.32-7.26 (m, 2H), 7.21 (d, J = 8.5 Hz, 2H), 3.51 (br s, 4H), 2.49 (s, 6H); ^{13}C NMR (C_6D_6, 100 MHz): δ 246.22, 138.74, 134.26, 134.08, 132.79, 129.73, 128.93, 127.86, 127.18, 125.84, 123.91, 52.49, 18.88.

1-Bromo-2,7-dimethylnaphthalene (1c). 25.93 g 2,7-dimethylnaphthalene were dissolved in 200 mL CH_2Cl_2, and then a 100 mL CH_2Cl_2 solution of Br_2 (1.0 eq.) was dropped into it over 1h at 0°C. After 3h the reaction was finished (confirmed by GC-MS). The reaction was quenched by adding a 200 mL of 25% $Na_2S_2O_3$ aqueous solution. The CH_2Cl_2 phase was separated and washed with 400 mL water, 400 mL 5% Na_2CO_3, dried by $MgSO_4$, filtered and concentrated under vacuum to afford light yellow crystals (38.65 g, 99%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (s, 1H), 7.67 (d, J = 5.0 Hz, 1H), 7.64 (d, J = 5.0 Hz, 1H), 7.29-7.24 (m, 2H), 2.60 (s, 3H), 2.55 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.38, 136.13, 132.84, 131.50, 128.1, 128.06, 127.99, 127.18, 126.14, 123.60, 24.40, 22.24. HRMS (EI) m/z calculated for $C_{12}H_{11}Br$ $[M]^+$ 234.0044, observed 234.0044.

N,N′-Bis(2,7-dimethylnaphthalen-1-yl)ethane-1,2-diamine (2c). A 100 mL two necked flask was charged with $Pd_2(dba)_3$ (65 mg, 0.07 mmol), (±)-BINAP (88 mg,

0.14 mmol), NaO^{t}Bu (410 mg, 4.26 mmol), 1-bromo-2,7-dimethylnaphthalene (**1c**) (700 mg, 2.98 mmol) and toluene (25 mL) in the glovebox. Ethylenediamine (95 μL, 1.42 mmol) were added by syringe outside the glovebox. The reaction mixture was stirred at 100°C for 16 h under nitrogen. When it cooled down, filtered through silica gel filter, washed with 300 mL hexane and the product was collected by washing with 400 mL CH_2Cl_2. The CH_2Cl_2 fraction was dried by rotavapor to give 517 mg (99%) of **2c** as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (s, 2H), 7.69 (d, J = 5.0 Hz, 2H), 7.43 (d, J = 5.0 Hz, 2H), 7.25-7.21 (m, 4H), 3.84 (br s, 2H), 3.44 (s, 4H), 2.49 (s, 6H), 2.45 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.67, 135.44, 132.01, 129.02, 128.71, 128.50, 127.36, 126.19, 122.97, 121.74, 50.69, 25.83, 22.35. HRMS (EI) m/z calculated for $C_{26}H_{28}N_2$ $[M]^+$ 368.2252, observed 368.2258.

1,3-Bis(2,7-dimethylnaphthalen-1-yl)-imidazolinium tetrafluoroborate (SIMeNap·HBF$_4$) (3c). Triethyl orthoformate (100 mL) was added to the diamine (**2c**) (3.22 g, 8.75 mmol) in a 250 mL Schlenk flask equipped with a distillation head. To this solution was added NH_4BF_4 (920 mg, 8.75 mmol) and 2 drops of formic acid. The reaction was heated to 100 °C and stirred for 12 h. Upon cooling to room temperature, the white precipitate was collected by filtration, washed with copious amounts of Et_2O and 2 × 5 mL CH_2Cl_2 and dried in vacuo to yield 3.47 g (85%) of the title product. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.42 (s, 0.45H), 9.39 (s, 0.55H) (corresponding to the two atropisomers of a single proton), 8.05-7.98 (m, 4.90H), 7.86 (s, 1.10H) (corresponding to the two atropisomers of six protons), 7.56-7.51 (m, 4H), 4.90-4.68 (m, 4H), 2.71 (s, 3H), 2.67 (s, 3H), 2.64 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz) (due to existence of two atropisomers, the ^{13}C NMR spectrum is complex): δ 162.24, 162.12, 138.52, 134.64, 131.31, 130.49, 130.01, 129.94, 129.08, 129.02, 128.90, 128.48, 128.39, 52.77, 52.68, 22.21, 18.12, 18.07. ^{19}F NMR ($CDCl_3$ 376.46 MHz): -152.82, -152.88. HRMS (ESI) m/z calculated for $C_{27}H_{27}N_2$ $[M\text{-}BF_4]^+$ 379.2174, observed 379.2179.

1,3-Bis(2,7-dimethylnaphthalen-1-yl)-imidazolinium chloride (SIMeNap·HCl) (3c′). The diamine (**2c**) (368 mg, 1.00 mmol) was dissolved in 6 mL THF, 7 mL 1.3M HCl solution was added at 0°C, and a white precipitation was obtained. The solid was filtered, dried under high vaccum, and then transferred into a 10 mL galss vial equipped with a stirring bar and charged with 2 mL triethyl orthoformate. The vial was capped and irradiated 5min at 145 °C in a CEM Discover instrument with a 50-W

microwave power. No ramp and no simultaneous cooling were applied. After rapid air-cooling by the unit, the reaction mixture was diluted with Et_2O (3 mL) and filtered under vacuum. The precipitate was rinsed with a few milliliters of Et_2O and dried under vacuum to afford a white powder (342 mg, 82%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.41 (s, 0.45H), 9.38 (s, 0.55H) (correspond to the two atropisomers of a single proton), 8.04-7.97 (m, 4.90H), 7.85 (s, 1.10H) (correspond to the two atropisomers of six protons), 7.55-7.50 (m, 4H), 4.89-4.67 (m, 4H), 2.70 (s, 3H), 2.66 (s, 3H), 2.63 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz) (due to existence of two atropisomers, ^{13}C NMR spectrum appeared complex): δ 161.73, 161.60, 138.03, 134.13, 130.81, 129.97, 129.93, 129.52, 129.45, 128.61, 128.55, 128.51, 128.04, 128.37, 127.98, 127.89, 120.36, 120.20, 52.33, 52.23, 21.69, 17.67, 17.62. HRMS (ESI) m/z calculated for $C_{27}H_{27}N_2$ $[M\text{-}Cl]^+$ 379.2174, observed 379.2179.

1,3-Bis(2,7-dimethylnaphthalen-1-yl)-imidazolin-2-ylidene (SIMeNap) (4c). A suspension of NaH (26 mg, 1.10 mmol) and KO^{t}Bu (6 mg, 5.00×10^{-2} mmol) in 10 mL THF was added into a suspension of SIMeNap·HBF_4 (**3c**) (466 mg, 1.00 mmol) in 10 mL THF. The reaction was stirred overnight at rt in the glovebox, filtered through celite and dried in vacuo to yield 348 mg (92%) of the white free carbene. Crystals suitable for an X-ray diffraction study were grown from an Et_2O solution. ^{1}H NMR (Toluene-d_8, 500 MHz): δ 8.02 (br s, 2H) 7.60 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 7.12 (dd, J = 8.3, 1.5 Hz, 2H), 3.52 (br s, 4H), 2.50 (br s, 6H), 2.42 (s, 6H). ^{13}C NMR (C_6D_6, 126 MHz): δ 245.97, 138.30, 136.57, 134.04, 133.10, 132.67, 128.89, 128.79, 127.99, 127.63, 123.24, 52.44, 22.69, 18.75.

1-Bromo-2,7-diisopropylnaphthalene (1d). 2.12 g 2,7-diisopropylnaphthalene were dissolved in 10 mL CH_2Cl_2, and then a 10 mL CH_2Cl_2 solution of Br_2 (1.0 eq.) was dropped into it over 0.5h at 0°C. After 1h the reaction was completed (confirmed by both TLC and GC-MS). The reaction was quenched by adding 10 mL of 25% $Na_2S_2O_3$ aqueous solution. The CH_2Cl_2 phase was separated and washed with 2 × 50 mL water, 2 × 50 mL 5% Na_2CO_3, dried by $MgSO_4$, filtered and concentrated under vacuum to afford a colorless oil (2.88 g, 99%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16 (s, 1H), 7.75 (d, J = 5.5 Hz, 1H), 7.73 (d, J = 5.5 Hz, 1H), 7.40 (dd, J = 8.7, 1.6 Hz, 2H), 7.38 (d, J = 8.7 Hz, 1H) 3.78 (sept, J = 7.0 Hz, 1H), 3.14 (sept, J = 7.0 Hz, 1H), 1.37 (d, J = 7.0 Hz, 6H), 1.32 (d, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.24, 145.33, 132.82, 132.15, 128.24, 127.3, 125.67, 124.47, 123.62, 123.15, 34.86,

34.06, 24.22, 23.10. HRMS (EI) m/z calculated for $C_{16}H_{19}Br$ $[M]^+$ 290.0670, observed 290.0673.

N,N′-Bis(2,7-diisopropylnaphthalen-1-yl)ethane-1,2-diamine (2d). A 250 mL schlenk flask was charged with $Pd_2(dba)_3$ (320 mg, 0.35 mmol), (±)-BINAP (523 mg, 0.84 mmol), NaO^tBu (2.02 g, 21.00 mmol), 1-bromo-2,7-diisopropylnaphthalene (**1d**) (4.08 g, 14.00 mmol) and toluene (150 mL) in the glovebox. Ethylenediamine (468 μL, 7.00 mmol) were added by syringe outside the glovebox. The reaction mixture was stirred at 110°C for 17 h under nitrogen. When it cooled down, filtered through silica gel filter, washed with hexane firstly and the product was collected by washing with CH_2Cl_2. The CH_2Cl_2 fraction was dried by rotavapor to give 3.04 g (90%) of **2d** as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14 (s, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.40-7.34 (m, 4H), 3.95 (s, 2H), 3.53 (sept, *J* = 6.6 Hz, 2H), 3.48 (s, 4H), 3.08 (sept, *J* = 6.6 Hz, 2H), 1.33 (br s, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.40, 140.70, 137.38, 132.03, 129.65, 128.48, 125.04, 123.78, 123.56, 119.98, 52.13, 34.84, 28.04, 24.33, 24.15. HRMS (EI) m/z calculated for $C_{34}H_{44}N_2$ $[M]^+$ 480.3504, observed 480.3504.

1,3-Bis(2,7-diisopropylnaphthalen-1-yl)-imidazolinium tetrafluoroborate (SIPrNap·HBF$_4$) (3d). Triethyl orthoformate (60 mL) was added to the diamine (**2d**) (2.02 g, 4.20 mmol) in a 100 mL schlenk flask equipped with a distillation head. To this solution was added NH_4BF_4 (440 mg, 4.20 mmol) and 2 drops of formic acid. The reaction was heated to 100 °C and stirred for 12 h. Upon cooling to rt, the white precipitate was collected by filtration, washed with a lot of Et_2O and 2 × 3 mL CH_2Cl_2 and dried in vacuo to yield 1.65 g (68%) of the title product. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.62 (s, 0.45H), 9.60 (s, 0.55H) (correspond to the two atropisomers of a single proton), 8.15 (dd, *J* = 8.8, 2.8 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), {7.89 (s, 0.90H), 7.73-7.68 (m, 3.10H) (correspond to the two atropisomers of four protons)}, 7.66-7.61 (m, 2H), 5.02-4.66 (m, 4H), 3.57 (sept, *J* = 6.7 Hz, 1H), 3.38 (sept, *J* = 6.8 Hz, 1H), 3.31 (sept, *J* = 6.7 Hz, 1H), 3.23 (sept, *J* = 6.8 Hz, 1H), 1.50 (d, *J* = 6.8 Hz, 3H), 1.46 (d, *J* = 6.8 Hz, 3H) 1.41 (d, *J* = 6.8 Hz, 6H), 1.38-1.36 (m, 6H), 1.29 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (DMSO-d_6, 125 MHz) (due to existence of two atropisomers, ^{13}C NMR spectrum appeared complex): δ 161.53, 161.43, 148.97, 144.19, 144.17, 131.11, 130.72, 129.32, 129.28, 128.81, 128.75, 126.76, 126.66, 126.23, 125.69, 123.45, 118.03, 117.27, 53.54, 53.38, 34.22, 33.96, 28.53, 24.16, 24.13, 24.06, 23.55.

^{19}F NMR ($CDCl_3$, 376.46 MHz): -153.40, -153.45. HRMS (ESI) m/z calculated for $C_{35}H_{43}N_2$ $[M\text{-}BF_4]^+$ 491.3426, observed 491.3420.

1,3-Bis(2,7-diisopropylnaphthalen-1-yl)-imidazolinium chloride (SIPrNap·HCl) (3d′). The diamine (**2d**) (481 mg, 1.00 mmol) was dissolved in 4 mL THF, 7 mL 1.3M HCl solution was added at 0°C, and a white precipitation was obtained. The solid was filtered, dried under high vaccum, and then transferred into a 10 mL galss vial equipped with a stirring bar and charged with 1.2 mL triethyl orthoformate. The vial was capped and irradiated 5min twice at 145 °C in a CEM Discover instrument with a 50-W microwave power. No ramp and no simultaneous cooling were applied. After rapid air-cooling by the unit, the reaction mixture was diluted with Et_2O (3 mL) and filtered under vacuum. The precipitate was rinsed with a few milliliters of Et_2O and dried under vacuum to afford a white powder (253 mg, 48%). Crystals suitable for diffraction study were grown from a CH_3Cl/Et_2O solution. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.63 (s, 0.45H), 9.60 (s, 0.55H) (correspond to two atropisomers of a single proton), 8.14 (dd, J = 8.7, 3.3 Hz, 2H), 8.05 (dd, J = 8.4, 1.2 Hz, 2H), {7.89 (s, 0.90H), 7.73-7.68 (m, 3.10H) (correspond to the two atropisomers of four protons)}, 7.66-7.61 (m, 2H), 5.05-4.65 (m, 4H), 3.57 (sept, J = 6.8 Hz, 1H), 3.38 (sept, J = 6.8 Hz, 1H), 3.30 (sept, J = 6.8 Hz, 1H), 3.23 (sept, J = 6.8 Hz, 1H), 1.50 (d, J = 6.8 Hz, 3H), 1.46 (d, J = 6.8 Hz, 3H) 1.41 (d, J = 6.8 Hz, 6H), 1.38-1.36 (m, 6H), 1.29 (d, J = 6.8 Hz, 6H). ^{13}C NMR (DMSO-d_6, 125 MHz) (due to existence of two atropisomers, ^{13}C NMR spectrum appeared complex): δ 161.53, 161.43, 148.97, 144.18, 144.16, 131.11, 131.09, 130.72, 130.70, 129.32, 129.27, 128.80, 128.74, 128.42, 126.76, 126.66, 126.22, 125.68, 123.46, 123.44, 118.03, 117.27, 53.54, 53.38, 34.21, 33.95, 28.53, 28.52 24.15, 24.12, 24.06, 24.04, 23.54, 23.11, 23.09, 23.04. HRMS (ESI) m/z calculated for $C_{35}H_{43}N_2$ $[M\text{-}Cl]^+$ 491.3426, observed 491.3426.

1,3-Bis(2,7-diisopropylnaphthalen-1-yl)-imidazolin-2-ylidene (SIPrNap) (4d). A suspension of NaH (26 mg, 1.10 mmol) and KO^{t}Bu (6 mg, 5.00×10^{-2} mmol) in 10 mL THF was added into a suspension of SIPrNap·HBF_4 (**3d**) (578 mg, 1.00 mmol) in 10 mL THF. The reaction was stirred for 24 h at rt in the glovebox, filtered through celite and dried in vacuo to yield 481 mg (98%) of the white free N-heterocyclic carbene. Crystals suitable for diffraction study were grown from an Et_2O/pentane solution. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.16 (s, 0.9H), 8.07 (s, 1.1H) (correspond to the two atropisomers of two protons), 7.74-7.68 (m, 4H), {7.40 (d, J = 8.5 Hz, 0.9H),

7.39 (d, J = 8.5 Hz, 1.1H) (correspond to the two atropisomers of two protons)}, 7.31 (dd, J = 8.3, 1.5 Hz, 0.9H), 7.27 (dd, J = 8.3, 1.5 Hz, 1.1H) (correspond to the two atropisomers of two protons), 3.91-3.80 (m, 2H), 3.76-3.66 (m, 2H), {3.55-3.48 (m, 1.1H), 3.41-3.39 (m, 0.9) (correspond to the two atropisomers of two protons)}, 3.15-3.02 (m, 2H), 1.50-1.34 (m, 24H). ^{13}C NMR (C_6D_6, 100 MHz) (due to existence of two atropisomers, ^{13}C NMR spectrum appeared complex): 246.29, 245.49, 147.38, 147.35, 144.26, 137.07, 133.10, 132.89, 132.85, 129.09, 128.95, 126.05, 125.39, 124.11, 124.05, 121.04, 120.42, 53.91, 53.78, 35.62, 35.31, 29.48, 29.42, 25.17, 25.08, 24.77, 24.66, 24.62, 24.31, 24.17, 24.01.

N,N′-Bis(anthracen-9-yl)ethane-1,2-diamine (2e). A 250 mL schlenk flask was charged with $Pd(dba)_2$ (383 mg, 0.67 mmol), (±)-BINAP (423 mg, 0.68 mmol), NaO^tBu (1.92 g, 20.00 mmol), 9-bromoanthracene (3.60 g, 14.00 mmol), ethylenediamine (445 μL, 6.67 mmol) and toluene (100 mL) in the glovebox. The reaction mixture was stirred at 110°C for 18 h under nitrogen. When it cooled down, it was filtered through a silica gel filter, washed with CH_2Cl_2, concentrated by rotavapor, and the residue was purified by flash chromatography (SiO_2, 1:1 CH_2Cl_2/hexane) to yield a yellow solid (1.76 g, 64%). ^{1}H NMR ($CDCl_3$ 400 MHz): δ 8.33 (m, 4H), 8.21 (m, 2H), 8.02 (m, 4H), 7.44 (m, 8H), 4.58 (br s, 2H), 3.66 (s, 4H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 141.32, 132.55, 129.25, 125.77, 125.48, 125.28, 123.11, 122.12, 52.68. HRMS (EI) m/z calculated for $C_{30}H_{24}N_2$ $[M]^+$ 412.1939, observed 412.1946.

1,3-Bis(anthracen-9-yl)-imidazolinium tetrafluoroborate (SIAnt·HBF$_4$) (3e). Triethyl orthoformate (25 mL) was added to the diamine (**2e**) (1.00 g, 2.42 mmol) in a 50 mL schlenk flask equipped with a distillation head. To this solution was added NH_4BF_4 (267 mg, 2.54 mmol) and 2 drops of formic acid. The reaction was heated to 100 °C and stirred for 30 min, then 150 °C for 1.5 h. Upon cooling to room temperature, the pale yellow precipitate was collected by filtration, washed with copious amounts of Et_2O and dried in vacuo to yield 883 mg (71%) of the title product. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.81 (s, 1H), 9.00 (s, 2H), 8.64 (d, J = 8.8 Hz, 4H), 8.33 (d, J = 8.7 Hz, 4H), 7.95 (dd, J = 8.8, 6.7 Hz, 4H), 7.76 (dd, J = 8.7, 6.7 Hz, 4H), 5.12 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 163.15, 131.10, 130.31, 129.10, 128.85, 127.76, 126.37, 125.95, 121.83, 54.09. ^{19}F NMR (DMSO, 376.49): -

148.27, -148.32. HRMS (ESI) m/z calculated for $C_{31}H_{23}N_2$ $[M\text{-}BF_4]^+$ 423.1861, observed 423.1851.

1,3-Bis(anthracen-9-yl)-imidazolidene (SIAnt) (4e). A suspension of NaH (26 mg, 1.10 mmol) and KO^{t}Bu (6 mg, 5.00×10^{-2} mmol) in 10 mL THF was added into a suspension of SIAnt·HBF_4 (**3e**) (510 mg, 1.00 mmol) in 10 mL THF. The reaction was stirred for 18 h at rt in the glovebox, filtered through celite and dried in vacuo to yield 380 mg (90%) of the pale green, free carbene. ^{1}H NMR (C_6D_6, 400 MHz): 8.63 (d, J = 8.7 Hz, 4H), 8.17 (s, 2H), 7.83 (d, J = 8.5 Hz, 4H), 7.43 (dd, J = 8.7, 6.5 Hz, 4H), 7.28 (dd, J = 8.5, 6.5 Hz, 4H), 3.79 (s, 4H). ^{13}C NMR (C_6D_6, 400 MHz): 248.21, 136.80, 133.08, 130.14, 129.49, 127.37, 127.01, 125.94, 124.54, 54.46.

Allylchloro[1,3-bis(2-methylnaphthalen-1-yl)-imidazolin-2-ylidene]palladium [(SI2MeNap)Pd(allyl)Cl] (5b): 4b (280 mg, 0.80 mmol) and $[Pd(allyl)Cl]_2$ (146 mg, 0.40 mmol) were mixed together in a vial in the glovebox. Dry THF (20 mL) was added and the mixture was stirred at room temperature for 12 h. The solvent was decanted, the solid was washed with 5 mL cold THF, and dried *in vacuo*. The crude product was dissolved in 10 mL CH_2Cl_2 and filtered through a celite filter to remove traces of palladium black. The white powder **5b** was obtained as a 1:1 mixture of the two atropisomers bearing *meso*- and *rac*-**4b** respectively (325 mg, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05-7.76 (m, 6H), 7.66-7.58 (m, 2H), 7.50-7.40 (m, 4H), 4.34-4.17 (m, 4H), 4.48-4.45 (m, 0.2H), 4.08-3.96 (m, 0.8H), (corresponding to the atropisomers of one proton), 3.53 (d, J = 7.5, 0.2H), 3.45 (d, J = 7.5, 0.8H), (corresponding to the atropisomers of one proton), 3.03 (d, J = 6.6, 0.5H), 3.45 (d, J = 6.6, 0.5H), (corresponding to the atropisomers of one proton), 2.88 (s, 1.5H), 2.76 (s, 3H), 2.74 (s, 1.5H), (corresponding to the atropisomers of six protons), 2.37-2.27 (m, 1H), 1.62 (d, J = 12.2 Hz, 0.2H), 1.10 (d, J = 12.2 Hz, 0.8H) (corresponding to the atropisomers of one proton). ^{13}C NMR ($CDCl_3$, 100 MHz) (due to the existence of the atropisomers, the ^{13}C NMR spectrum is complex): 214.45, 214.34, 213.99, 136.32, 136.08, 134.80 (two signals overlapped), 134.53, 134.36, 134.25, 133.38, 133.31, 133.25, 131.07, 131.01, 130.89, 129.98, 129.92, 129.14, 129.09, 128.92, 128.87.128.79, 128.74, 128.33 (two signals overlapped), 127.06, 126.98, 126.91, 126.58, 125.90 (two signals overlapped), 125.52, 125.39, 123.54 (two signals overlapped), 122.30, 122.21, 114.77, 114, 66, 72.25, 72.17, 72.06, 52.42, 52.29,

52.25, 51.11, 50.51, 49.78, 19.54, 19.50, 19.22, 19.15. HRMS (ESI) m/z calculated for $C_{28}H_{27}PdN_2$ $[M\text{-}Cl]^+$ 495.1210, observed 495.1211.

Allylchloro[1,3-bis(2,7-dimethyl-naphthalen-1-yl)-imidazolin-2-ylidene]palladium [(SIMeNap)Pd(allyl)Cl] (5c): 4c (930 mg, 2.46 mmol) and $[Pd(allyl)Cl]_2$ (449 mg, 1.23 mmol) were mixed together in a vial in the glovebox. Dry THF (20 mL) was added and the mixture was stirred at room temperature for 1.5 h. The solvent was removed *in vacuo*, and 20 mL of hexane was added to triturate the product. The reaction mixture was filtered in air and the solid washed with hexane. The two isomers were successfully separated by repeated fractional crystallization with CH_2Cl_2/hexane to yield 662 mg of **5c**$_{meso}$ (48% yield) and 400 mg of **5c**$_{rac}$ (23% yield). Crystals suitable for diffraction studies were grown from CH_2Cl_2/hexane solutions.

Data for **5c**$_{meso}$ are as follows. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.70 (m, 6H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.32-7.29 (m, 2H), 4.29-4.24 (m, 4H), 4.05-3.95 (m, 1H), 3.45 (dd, *J* = 7.5, 2.5 Hz, 1H), 2.87-2.85 (m, 1H), 2.81 (s, 3H), 2.72 (s, 3H), 2.59 (s, 6H), 2.29 (d, *J* = 12.2 Hz, 1H), 1.11 (d, *J* = 12.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): 214.27, 136.34, 136.30, 136.14, 136.01, 133.95, 133.68, 131.58, 131.17, 131.05, 129.11, 129.09, 129.08, 129.06, 128.77, 128.49, 128.43, 127.63, 127.49, 121.57, 121.42, 114.66, 71.89, 52.17, 52.11, 50.79, 22.62, 19.51,19.49. HRMS (ESI) m/z calculated for $C_{30}H_{31}PdN_2$ $[M\text{-}Cl]^+$ 523.1523, observed 523.1528.

Data for **5c**$_{rac}$ are as follows. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.70 (m, 6H), 7.36-7.33 (m, 2H), 7.30-7.26 (m, 2H), 4.35-4.31 (m, 0.4H), 4.23 (s, 4H), 4.14-4.04 (m, 0.6H), 3.51 (dd, *J* = 7.5, 2.5 Hz, 0.4H), 3.44 (dd, *J* = 7.5, 2.5 Hz, 0.6H), 3.09 (dd, *J* = 6.6, 2.0 Hz, 0.6H), 3.05 (dd, *J* = 6.6, 2.0 Hz, 0.4H), 2.79 (s, 1.2H), 2.78 (s, 1.8H), 2.59 (s, 1.8H), 2.57 (s, 1.2H), 2.29-2.26 (m, 1H), 1.57, (d, *J* = 1.8 Hz, 0.6H), 1.26 (d, *J* = 1.8 Hz, 0.4H). ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of two isomers, ^{13}C NMR spectrum appeared complex): 214.58, 214.16, 136.67, 136.66, 134.32, 134.31, 134.09, 131.69, 131.66, 131.21, 131.19, 128.63, 128.58, 128.09, 128.04, 122.98, 122.90, 114.64, 72.17, 72.02, 52.41, 49.87, 49.33, 22.50, 19.08, 18.99. HRMS (ESI) m/z calculated for $C_{30}H_{31}PdN_2$ $[M\text{-}Cl]^+$ 523.1523, observed 523.1528.

Allylchloro[1,3-bis(2,7-diisopropylnaphthalen-1-yl)-imidazolin-2-ylidene]palladium [(SIPrNap)Pd(allyl)Cl] (5d): 4d (1.02 g, 2.07 mmol) and $[Pd(allyl)Cl]_2$ (377 mg, 1.03 mmol) were mixed together in a round bottom flask in the glovebox. Dry THF (50 mL) was added and the mixture was stirred at room temperature for 1.5 h. The solvent was removed *in vacuo*, and 30 mL of hexane was added to triturate the product. The reaction mixture was filtered in air and the solid washed with hexane. The two isomers were successfully separated by fractional crystallization with EtOAc/hexane to yield 585 mg of $\mathbf{5d}_{meso}$ (42% yield) and 544 mg of $\mathbf{5d}_{rac}$ (36% yield).

Data for $\mathbf{5d}_{meso}$ are as follows. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86-7.73 (m, 6H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.45-7.38 (m, 2H), 4.35-4.20 (m, 4H), 4.16-4.08 (m, 1H), 3.83, (sept, *J* = 6.8 Hz, 1H), 3.68, (sept, *J* = 6.8 Hz, 1H), 3.48 (dd, *J* = 7.5, 2.0 Hz, 1H), 3.21-3.13 (m, 2H), 2.87-2.85 (m, 1H), 2.35 (d, *J* = 13.4 Hz, 1H), 1.61-1.22 (m, 24H), 1.10 (d, *J* = 12.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): 213.97, 147.38, 146.87, 146.22, 145.70, 133.09, 132.78, 132.02, 131.87, 130.89, 130.30, 129.15, 129.14, 129.12, 124.47, 124.45, 124.33, 123.89, 120.38, 120.05, 114.48, 71.56, 60.60, 53.92, 53.59, 51.08, 35.90, 35.70, 31.80, 29.01, 28.90, 26.04, 26.01, 24.93, 24.83, 24.15, 24.11, 24.03, 24.01, 23.67, 22.87, 21.26, 14.42, 14.32. HRMS (ESI) m/z calculated for $C_{30}H_{31}PdN_2ClNa$ $[M+Na]^+$ 693.2361, observed 693.2373.

Data for $\mathbf{5d}_{rac}$ are as follows. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86-7.75 (m, 6H), 7.47-7.38 (m, 4H), 4.64-4.59 (m, 0.8H), 4.35-4.29 (m, 4H), 4.08-4.01 (m, 0.2H), 2.90-3.82 (m, 2H), 3.60 (dd, *J* = 7.5, 2.4 Hz, 0.8H), 3.51 (dd, *J* = 7.5, 2.4 Hz, 0.2H), 3.16 (sept, *J* = 6.8, 2H), 2.95-2.93 (m, 0.8H), 2.79-2.77 (m, 0.2H), 2.48-2.42 (m, 1H), 1.78 (d, *J* = 11.9 Hz, 0.2H), 1.50-1.36 (m, 24H), 0.78 (d, *J* = 11.9 Hz, 0.8H). ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of two isomers, ^{13}C NMR spectrum appeared complex): 214.38, 213.27, 147.12, 147.06, 144.69, 144.51, 133.17, 133.10, 131.93, 131.83, 131.02, 130.99, 129.25, 129.22, 128.29, 128.21, 126.40, 126.21, 123.51, 123.47, 120.43, 120.35, 114.62, 114.58, 72.58, 52.27, 53.69, 53.63, 50.24, 49.69, 34.65, 34.61, 28.88, 28.82, 25.91, 25.63, 24.10, 23.94, 23.87, 23.71, 23.66, 23.54. HRMS (ESI) m/z calculated for $C_{30}H_{31}PdN_2ClNa$ $[M+Na]^+$ 693.2361, observed 693.2373.

{$RuCl_2$[1,3-bis(2-methylnaphthalen-1-yl)-imidazolin-2-ylidene](=CH-Ph)(PCy_3)} [$RuCl_2$(SI2MeNap)(=CHPh)(PCy_3)] (6b): 4b (300 mg, 0.85 mmol) and $RuCl_2$(=C(H)Ph)(PCy_3)$_2$ (700 mg, 0.85 mmol) were mixed together in a 200 mL flask in the glovebox. Dry toluene (40 mL) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo*, washed with 4 × 10 mL hexane, and then dissolved in minimum CH_2Cl_2 and precipitated with Et_2O/pentane (1:3). Filtration of the pink precipitate afforded the product **6b** in 65% (495 mg) yield. ^{1}H NMR (CD_2Cl_2, 400 MHz, 273K) exists as a mixture of atropisomers: δ 19.04 (s, Ru=C*H*Ph), 19.01 (s, Ru=C*H*Ph), 18.48 (s, Ru=C*H*Ph), 18.45 (s, Ru=C*H*Ph), (corresponding to the atropisomers of one proton), 8.87-6.09 (m, Ar*H*, 17H), 4.31-3.93 (m, NCH_2CH_2N, 4H), 3.44-2.33 (m, ArCH_3, 6H), 1.93-0.40 (m, P*Cy*$_3$, 33H). ^{13}C NMR (CD_2Cl_2, 100 MHz, 300K) (due to the existence of the atropisomers, the ^{13}C NMR spectrum is complex): δ 294.92, 222.61, 221.85, 151.19, 138.15, 137.78, 136.46, 135.80, 134.37, 133.89, 133.36, 133.33, 132.04, 131.88, 131.36, 131.18, 130.22, 130.20, 129.94, 129.38, 129.20, 129.12, 128.18, 128.12, 128.04, 127.95, 127.25, 127.09, 126.92, 126.50, 126.21, 126.19, 125.69, 124.77, 121.51, 31.98, 31.96, 31.81, 31.79, 29.41, 29.23, 28.27, 28.23, 28.16, 28.06, 26.65, 21.16, 21.04, 19.49, 19.31. ^{31}P NMR (CD_2Cl_2, 162 MHz, 273K): δ 30.96, 30.48, 29.92. HRMS (ESI) m/z calculated for $C_{50}H_{60}PRuN_2$ [M-2Cl-H]$^+$ 815.3571, observed 815.3556.

{$RuCl_2$[1,3-bis(2,7-dimethyl-naphthalen-1-yl)-imidazolin-2-ylidene](=CH-Ph)(PCy_3)} [$RuCl_2$(SIMeNap)(=CHPh)(PCy_3)] (6c): 4c (322 mg, 0.85 mmol) and $RuCl_2$(=C(H)Ph)(PCy_3)$_2$ (700 mg, 0.85 mmol) were mixed together in a 200 mL flask in the glovebox. Dry toluene (40 mL) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo*, washed with 4 × 10 mL hexane, and then dissolved in minimum CH_2Cl_2 and precipitated with Et_2O/pentane (1:3). Filtration of the pink precipitate afforded the product **6c** in 73% (575 mg) yield. ^{1}H NMR (CD_2Cl_2, 400 MHz, 260K) exists as a mixture of atropisomers: δ 18.97 (s, Ru=C*H*Ph), 18.94 (s, Ru=C*H*Ph), 18.44 (s, Ru=C*H*Ph), 18.40 (s, Ru=C*H*Ph), (corresponding to the atropisomers of one proton), 9.09-6.08 (m, Ar*H*, 15H), 4.25-3.88 (m, NCH_2CH_2N, 4H), 3.05-2.22 (m, ArCH_3, 12H), 1.92-0.36 (m, P*Cy*$_3$, 33H). ^{13}C NMR (CD_2Cl_2, 100 MHz, 273K) (due to the existence of the atropisomers, the ^{13}C NMR spectrum is complex): δ 295.99, 294.61, 293.95, 293.51, 223.50, 222.74, 221.87, 221.52, 221.11, 160.66, 160.45, 151.32, 150.56, 150.45,

139.75, 139.56, 137.37, 136.82, 136.58, 136.18, 135.90, 135.78, 135.63, 135.34, 135.06, 134.81, 134.52, 133.57, 133.36, 132.19, 131.84, 131.61, 131.50, 131.24, 130.68, 130.03, 129.75, 129.61, 129.35, 129.28, 129.15, 129.09, 128.81, 128.61, 128.21, 128.09, 127.76, 127.56, 126.87, 126.29, 126.21, 124.43, 123.87, 123.27, 122.90, 119.86, 34.55, 32.05, 31.53, 31.39, 31.24, 29.25, 29.12, 28.83, 28.55, 25.05, 27.96, 27.87, 26.44, 23.13, 22.83, 22.57, 22.43, 22.25, 20.82, 19.31, 19.06, 18.91, 14.41, 14.35. ^{31}P NMR (CD_2Cl_2, 162 MHz, 270K): δ 30.45, 29.48, 29.09. HRMS (ESI) m/z calculated for $C_{52}H_{64}PRuN_2$ $[M\text{-}2Cl\text{-}H]^+$ 843.3883, observed 843.3878.

{$RuCl_2$[1,3-bis(2,7-diisopropyl-naphthalen-1-yl)-imidazolin-2-ylidene](=CH-Ph)(PCy_3)} [$RuCl_2$(SIPrNap)(=CHPh)(PCy_3)] (6d): 4d (170 mg, 0.35 mmol) and $RuCl_2$(=C(H)Ph)(PCy_3)$_2$ (277 mg, 0.34 mmol) were mixed together in a vial in the glovebox. Dry toluene (19 mL) was added and the mixture was stirred at room temperature for 28 h. After transferring it into a flask, the solvent was removed *in vacuo*. The content was dissolved in diethyl ether and filtered over cotton (6 mL total). Then, methanol was layered on top of it (14 mL) and the vial was put into the freezer for 6 h. The precipitate was taken out of the freezer and left at room temperature for an additional hour. Then, the mother liquor was decanted off and precipitation was repeated once more (4 mL diethylether/15 mL methanol). Decantation was followed by drying *in vacuo*. From the combined mother liquors, another crop of pure pink product was obtained. Combined yield: 81% (280 mg). ^{1}H NMR (CD_2Cl_2, 400 MHz, 300K) exists as a mixture of atropisomers: δ 19.23 (s, Ru=C*H*Ph), 19.20 (s, Ru=C*H*Ph), (corresponding to the atropisomers of one proton), 8.56-6.66 (m, Ar*H*, 15H), 4.42-3.14 (m, NCH_2CH_2N + ArC*H*$(CH_3)_2$, 8H), 1.98-0.56 (m, ArCH_3 + P*Cy*$_3$, 57H). ^{13}C NMR (CD_2Cl_2, 100 MHz, 300K) (due to the existence of the atropisomers, the ^{13}C NMR spectrum is complex): δ 294.58, 293.28, 222.82, 222.05, 150.77, 150.64, 147.58, 147.21, 146.66, 146.48, 145.23, 144.98, 135.28, 135.10, 133.14, 132.99, 132.57, 131.96, 131.83, 131.76, 131.53, 131.25, 131.21, 130.48, 130.42, 129.54, 129.50, 128.15, 128.10, 127.88, 127.62, 126.61, 125.89, 125.58, 124.96, 124.17, 124.12, 124.07, 123.21, 123.16, 122.39, 120.85, 54.72, 51.00, 35.53, 35.45, 35.07, 34.80, 32.10, 32.01, 31.94, 31.84, 29.86, 29.74, 29.30, 29.24, 29.02, 28.57, 28.53, 28.26, 28.16. 28.07, 26.70, 26.46, 25.93, 25.83, 24.65, 24.58, 24.54, 24.17, 24.05, 23.39, 23.23, 23.14, 22.86. ^{31}P NMR (CD_2Cl_2, 162 MHz, 300K):

δ 29.49, 29.22. HRMS (ESI) m/z calculated for $C_{60}H_{80}PRuN_2$ $[M\text{-}2Cl\text{-}H]^+$ 961.5096, observed 961.5107.

Suzuki-Miyaura Cross-Coupling Reactions: General Procedure. In a glovebox, to a vial closed with a screw cap fitted with a septum and equipped with a magnetic stir bar were added in turn catalyst (1.00 mol %), potassium *tert*-butoxide (124 mg, 1.10 mmol), boronic acid (1.05 mmol), 2-propanol (1 mL) and dodecane (216 μL, 1.00 mmol). The mixture was then stirred at room temperature. After 15 min, the aryl chloride (1.00 mmol) was injected. If the reaction was carried out at 80 °C, the aryl chloride was injected outside the glovebox. The reaction was monitored by gas chromatography, and the yields were determined through integration of the product against dodecane (internal standard) using pre-established response factors.

2'-Methyl-2-methoxybiphenyl (Table 3, entries 1-10):[33] t_R = 11.84 min (80 °C, 3 min, 15 °C/min).

1-(4-Methylphenyl)naphthalene (Table 3, entries 11-20):[34] t_R = 14.79 min (80 °C, 3 min, 15 °C/min).

Hartwig-Buchwald Cross-Coupling Reactions. General Procedure. In a glovebox, to a vial closed with a screw cap fitted with a septum and equipped with a magnetic stir bar were added in turn catalyst (1.00 mol %), potassium *tert*-butoxide (124 mg, 1.10 mmol), anhydrous DME (1 mL), and dodecane (216 μL, 1.00 mmol). The mixture was then stirred at room temperature. After 5 min, the aryl chloride (1.00 mmol) and the amine (1.10 mmol) were injected. If the reaction was carried out at 80 °C, the aryl chloride and the amine were injected outside the glovebox. The reaction was monitored by gas chromatography, and the yields were determined through integration of the product against dodecane (internal standard) using pre-established response factors.

Hartwig-Buchwald Cross-Coupling Reactions at Low Catalyst Loading. In a glovebox, 0.01 mmol of complex (6.7 mg of **5d**) was dissolved in 10 mL DME, providing catalyst solution A. To another vial closed with a screw cap fitted with a septum and equipped with a magnetic stir bar were added in turn potassium *tert*-butoxide (124 mg, 1.10 mmol), catalyst solution A (1 mL, 0.1 mol %), and dodecane (216 μL, 1.00 mmol). The mixture was then stirred at room temperature. After 5 min,

the aryl chloride (1.00 mmol) and the amine (1.10 mmol) were injected. The reaction was monitored by gas chromatography, and the yields were determined through integration of the product against dodecane (internal standard) using pre-established response factors.

N-(2-pyridyl)morpholine (Table 3, entries 21-26):[35] t_R = 10.05 min (80 °C, 3 min, 15 °C/min).

N-(4-Methylphenyl)piperidine (Table 3, entries 27-31):[36] t_R = 11.31 min (80 °C, 3 min, 15 °C/min).

RCM of diethyldiallyl malonate in the presence of 1 mol% of catalyst. An NMR tube with screw-cap sample top was charged inside the glove box with 0.80 ml of CD_2Cl_2 catalyst solution 0.0010 M (0.80 μmol, 1.0 mol%). The sample was equilibrated at 300 K in the NMR instrument before the substrate (19.3 μl, 19.2 mg, 0.080 mmol) was added via syringe. Data points were collected after an appropriate period of time. The conversion was determined by comparing the ratio of the integrals of methylene protons in the starting material, δ 2.61(dt), with those in the product, δ 2.98(s).

RCM of diethyldiallyl malonate in the presence of 0.1 mol% of catalyst. An NMR tube with screw-cap sample top was charged inside the glove box with 0.080 ml of CD_2Cl_2 catalyst solution 0.0010 M (0.080 μmol, 0.1 mol%) and 0.72 ml of CD_2Cl_2. The sample was equilibrated at 300 K in the NMR instrument before the substrate (19.3 μl, 19.2 mg, 0.080 mmol) was added via syringe.

RCM of linalool in the presence of 1 mol% of catalyst. An NMR tube with screw-cap sample top was charged inside the glove box with 0.80 ml of CD_2Cl_2 catalyst stock solution 0.0010 M (0.80 μmol, 1.0 mol%). The sample was equilibrated at 300 K in the NMR instrument before the substrate (14.3 μl, 12.3 mg, 0.080 mmol) was added via syringe. Data points were collected after an appropriate period of time. The conversion was determined by comparing the ratio of the integrals of methyl protons in the starting material, δ 1.24 (s), with those in the product, δ 1.34 (s).

RCM of linalool in the presence of 0.1 mol% of catalyst. An NMR tube with screw-cap sample top was charged inside the glove box with 0.080 ml of CD_2Cl_2 catalyst stock solution 0.0010 M (0.080 μmol, 0.1 mol%) and 0.72 ml of CD_2Cl_2. The

sample was equilibrated at 300 K in the NMR instrument before the substrate (14.3 μl, 12.3 mg, 0.080 mmol) was added via syringe.

RCM of N,N-diallyl-4-methyl-benzenesulfonamide in the presence of 1 mol% of catalyst. An NMR tube with screw-cap sample top was charged inside the glove box with 0.40 ml of a CD_2Cl_2 catalyst stock solution 0.0020 M (0.80 μmol). The sample was equilibrated at 300 K in the NMR instrument before 0.4 ml of a CD_2Cl_2 solution of the substrate (18.9 mg, 0.080 mmol) was added via syringe. Data points were collected after an appropriate period of time. The conversion was determined by comparing the ratio of the integrals of methylene protons in the starting material, δ 3.77(d), with those in the product, δ 4.08 (s).

RCM of N,N-diallyl-4-methyl-benzenesulfonamide in the presence of 0.1 mol% of catalyst. An NMR tube with screw-cap sample top was charged inside the glove box with 0.76 ml of a CD_2Cl_2 solution of the substrate (18.9 mg, 0.080 mmol). The sample was equilibrated at 300 K in the NMR instrument before 0.040 ml of a CD_2Cl_2 catalyst stock solution 0.0020 M (0.080 μmol) was added via syringe.

RCM of diethyl-2,2-di(2-methylallyl)malonate in the presence of 5 mol% of catalyst. An NMR tube with screw-cap sample top was charged inside the glove box with 0.40 ml of CD_2Cl_2 catalyst solution 0.010 M (0.004 mmol, 5.0 mol%) and 0.40 ml of CD_2Cl_2 solution of the substrate (21.5 mg, 0.08 mmol). The sample was kept at 300 K for 72h. The conversion was determined by comparing the ratio of the integrals of methylene protons in the starting material, δ 2.71(s), with those in the product, δ 2.90 (s).

General Reaction Procedure for the Alkylation of Meso Epoxides. All reactions were carried out in a glovebox, and the epoxides were dried over CaH_2 and stored inside a glovebox. Into a 20 mL vial equipped with a magnetic stir bar were added the epoxide (1.00 mmol), internal standard (30 mg, 0.22 mmol) and toluene (2 mL). Subsequently, the catalyst (1.00 mol %) and the triethylaluminum reagent (1.10 mL, 2.00 mmol) were added and the reaction was stirred at room temperature for 12-24 h.

The reaction was quenched with HCl (4 mL of a 1M solution in H_2O) and extracted with ether (3 x 5 mL). The combined organic extracts were washed successively with

brine (10 mL) and H_2O (10 mL) and dried over $MgSO_4$. The solution was filtered and an aliquot was analyzed by GC to determine the yield.

trans-2-Ethyl-1-cyclohexanol (Table 5, entries 4-6):[37] t_R = 6.49 min (80 °C, 10 °C/min).

trans-2-Ethyl-1-cyclopentanol (Table 5, entries 7-11):[38] t_R = 4.71 min (80 °C, 3 min, 10 °C/min).

anti-2-Hydroxy-3-methylpentane (Table 5, entries 12-16):[39] t_R = 8.08 min (40 °C, 6 min, 10 °C/min).

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Chapter 3

Matching the Chirality of Monodentate *N*-Heterocyclic Carbene Ligands: A Case Study on Well-Defined Palladium Complexes for the Asymmetric α-Arylations of Amides.

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3.1 Abstract

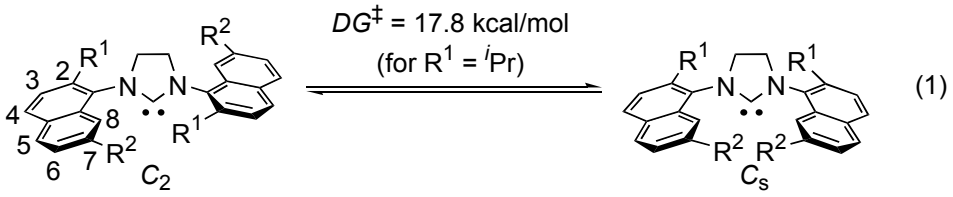
N-heterocyclic carbene ligands derived from C_2-symmetric diamines with naphthyl side chains are introduced as chiral monodentate ligands and their palladium complexes (NHC)Pd(cin)Cl are prepared. These compounds exist as a mixture of diastereomers, and the palladium complexes can be successfully separated and their absolute stereochemistry assigned. When used in the asymmetric intramolecular α-arylation of amides, oxindoles with quaternary carbon centers can be obtained in high yield and selectivity when correctly matching the chirality of the NHC complexes.

3.2 Introduction

N-heterocyclic carbenes often show increased reactivity and stability when compared to the commonly employed phosphine ligands.[1] Because of their tight metal binding and robustness, monodentate, chiral N-heterocyclic carbene ligands appear to be a very promising ligand class for asymmetric catalysis.[2] Development in this area has been relatively slow,[3-5] and versatile chiral NHCs remain elusive. Two reasons might account for this. First, the overwhelming majority of chiral NHC salts is deprotonated and used in situ,[6] a circumstance that precludes a detailed discussion on the reaction/selection pathway of a given transformation and hinders development of optimized ligand structures. Another problem consists in building chirality without losing the reactivity/versatility of the most successful achiral ligand architectures, which incorporate aromatic *N*-substituents (for instance IMes/SIMes and IPr/SIPr). Elegant work by Grubbs et al. has shown that NHCs derived from C_2-symmetric diamines and mono-*ortho*-substituted aryl halide side chains provide successful ligand systems in some ruthenium-catalyzed asymmetric metathesis reactions.[4] Similar architectures with unsymmetrically 2,6-disubstituted phenyl side chains have been reported more recently showing encouraging results.[5] In all of these cases, no mention is made regarding the possibly different orientations of the side chains or their ease of rotation with respect to the chiral *N*-heterocyclic backbone and the resulting impact on selectivity or reactivity in catalysis.[7]

In the course of studying a series of NHCs that incorporate 2-substituted naphthyl side chains,[8] we found that NHCs with R^1 = methyl/isopropyl have two atropisomers with C_2-symmetric (*anti* orientation of side chains) and C_s-symmetric (*syn*) conformations (eq 1). Logically, if the chiral regime of C_2-symmetric diamines

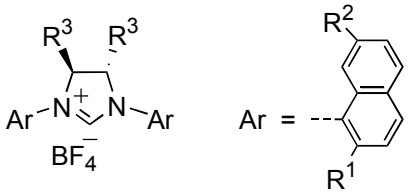
is introduced to the heterocyclic backbone of these NHCs, three diastereomers should be generated. Before embarking on the present study, we reasoned that ligand systems with bulky R^1 groups would be the best candidates because of their rotational stability (eq 1) and excellent catalytic behavior.[8] Moreover, building upon the successful separation of *anti/syn* palladium complexes in our previous study, we decided to concentrate our preliminary efforts on the palladium-catalyzed asymmetric intramolecular α-arylation of amides to give chiral quaternary carbon centers.[9]



(1)

3.3 Results and Discussion

To get the best insight possible into factors that govern the selectivity and reactivity of these new ligands, variations in both the chirality of the imidazolinium backbone (R^3) and the steric properties of the side chains (R^1 = isopropyl or cyclohexyl; R^2 = isopropyl or hydrogen) were introduced and four different NHC salts were prepared (Figure 1). Careful analysis of the *N*-heterocyclic proton signals by ^{1}H NMR showed three different diastereomers for all four ligands (**1a-d**).



mixture of three diastereomers

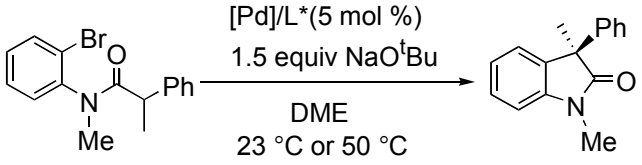
(*4S,5S*)-DiPhSIPrNap·HBF$_4$ (**1a**, $R^1 = R^2 = {}^i$Pr, R^3 = Ph) [**54**(R_a,R_a):**36**(R_a,S_a):**10**(S_a,S_a)]
(*4S,5S*)-DiPhSI2PrNap·HBF$_4$ (**1b**, $R^1 = {}^i$Pr, R^2 = H, R^3 = Ph) [**51**(R_a,R_a):**41**(R_a,S_a):**8**(S_a,S_a)]
(*4S,5S*)-DiPhSI2CyNap·HBF$_4$ (**1c**, R^1 = Cy, R^2 = H, R^3 = Ph) [**71**(R_a,R_a):**21**(R_a,S_a):**8**(S_a,S_a)]
(*4R,5R*)-CySIPrNap·HBF$_4$ [**1d**, $R^1 = R^2 = {}^i$Pr, R^3 = -(*R*,*R*)-$(CH_2)_4$-] (**45:40:15**)

Figure 1. New chiral *N*-Heterocyclic carbene precursors **1a-d**.

Ligand precursors **1a-d** were then tested in the intramolecular α-arylation of **3a** following Hartwig's *in situ* method (Table 1).[9a] Results showed that $Pd(dba)_2$, $Pd(OAc)_2$ as well as $[Pd(cin)Cl]_2$ (cin = cinnamyl) could be used as palladium sources. Although diastereomeric mixtures of ligands **1a-d** were employed, oxindole

4a was obtained with selectivities of up to 71% ee whith ligand **1a** (entry 1), whereas using **1d** resulted in almost racemic product (entry 6). This result already indicates that the chiral information is probably transferred to the substrate from the chiral diamine part of the *N*-heterocycle.

Table 1. Asymmetric intramolecular α-arylation of amide **3a** with **1a-d**/palladium source.

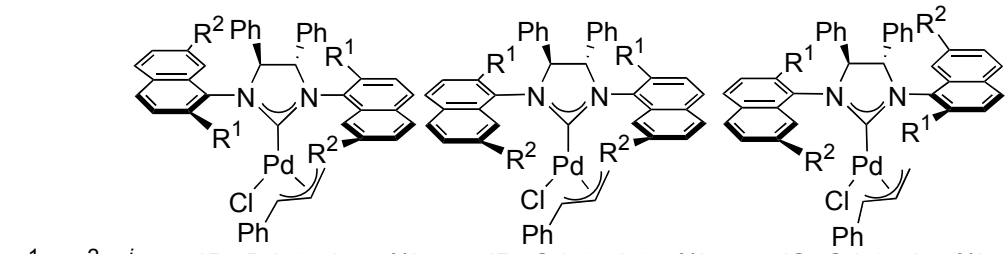


3a **4a**

entry	L*	[Pd]	*t* (°C)	time (h)	% yield[a] (% ee[b,c])
1	**1a**	$Pd(dba)_2$	23	12	98 (71)
2	**1a**	$[Pd(cin)Cl]_2$	23	12	98 (69)
3	**1a**	$Pd(OAc)_2$	23	24	96 (66)
4	**1b**	$Pd(dba)_2$	50	24	98 (59)
5	**1c**	$Pd(dba)_2$	50	24	91 (47)
6	**1d**	$Pd(dba)_2$	23	12	92 (–6)

[a]Isolated yields. [b]Determined by chiral HPLC. [c]Absolute stereochemistry determined as (*R*)-configuration, see ref. 9d.

Diastereomers of **1a-c** were then used for the synthesis of (NHC)Pd(cin)Cl complexes **2a-c**.[10,11] As expected from our previous studies on similar ligands (equation 1), crude mixtures of the complexes maintained the ratio between the diastereomers of the NHC salts. For all three compounds, we were able to separate these diastereomeric compounds via column chromatography and assign the absolute configurations unequivocally by using a combination of both NMR spectroscopy and X-ray structural determinations (Figure 2). The main *anti* ligand isomer orients its more hindered half of the naphthyl moiety onto the protruding phenyl ring of the backbone, an intriguing result in view of the previously assumed prevalence of (S_a,S_a)-isomers in this ligand class.[12] Numerous broad signals in the ^{1}H NMR spectra of **2a-c** reflect the important steric crowding and the resulting restricted rotation of both the cinnamyl and NHC side chains in these complexes. Nonetheless, very diagnostic upfield shifts are found for some of the R^1 protons and arise from strong σ-π interactions with the chiral backbone phenyl moieties. Together with the X-ray analyses and the proton signals of the N-heterocyclic backbone, the presence [twice for (R_a,R_a)-**2**, once for (R_a,S_a)-**2**] or absence [for (S_a,S_a)-**2**] of these upfield signals lead to the correct assignment of the different diastereomers.



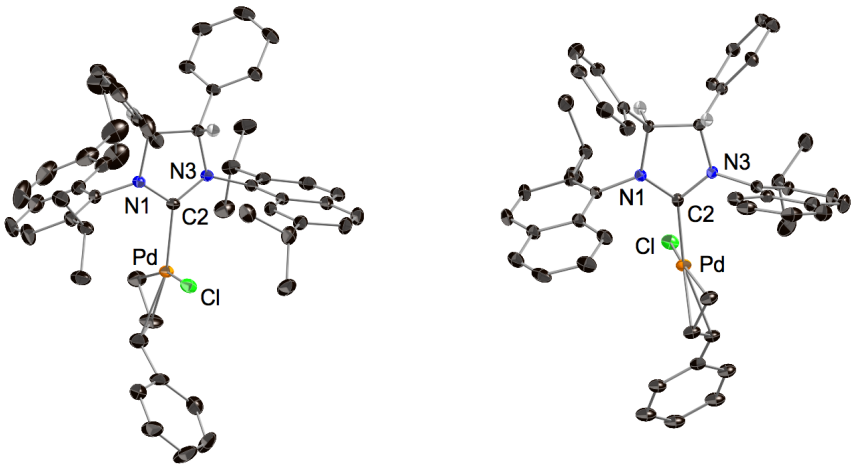
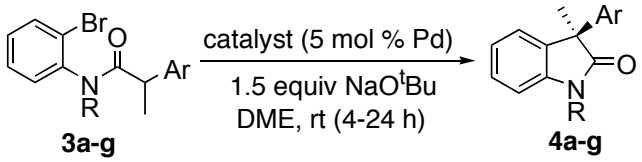


Figure 2. Complexes **2a-c** (above, yields in brackets) and X-rays of [(R_a,R_a)-(*4S*,*5S*)-DiPhSIPrNap]Pd(cin)Cl (below left, (R_a,R_a)-**2a**), and [(R_a,S_a)-(*4S*,*5S*)-DiPhSI2PrNap]Pd(cin)Cl (below right, (R_a,S_a)-**2b**).

The series of pure precatalysts was then applied to the asymmetric oxindole synthesis starting from different 2-bromoanilides and the catalytic results are given in Table 2. Yields of isolated products are excellent and reaction times of less than 24 hours were observed. Minor discrepancies in reactivity exist between catalysts (**2a** more active than **2b**/**2c**),[13] as well as between the three diastereomers of **2a** (see Supporting Information). On the other hand, selectivity differences are very pronounced and reflect the crucial importance of the ligand architecture. Precatalysts derived from the minor diastereomeric form of the ligands (S_a,S_a) failed to give products with more than 50% ee. Both (R_a,S_a)- and (R_a,R_a)-isomers proved superior in terms of selectivity. Enantiomeric excesses when the (R_a,S_a)-complexes were employed ranged from moderate (45% ee) to high (89% ee) and showed a marked substrate-dependence. Of all the precatalysts tested, (R_a,R_a)-**2a** outperformed its congeners and gave high and very evenly distributed chiral induction (80-88% ee) for all substrates. As such, (R_a,R_a)-**2a** compares well with the best systems described

recently by Kündig et al.,[9d] giving generally better yields and slightly higher ee's in two cases (entries 10 and 18).

Table 2. Asymmetric intramolecular α-arylation of amides with **2a-c**.



3a-g **4a-g**

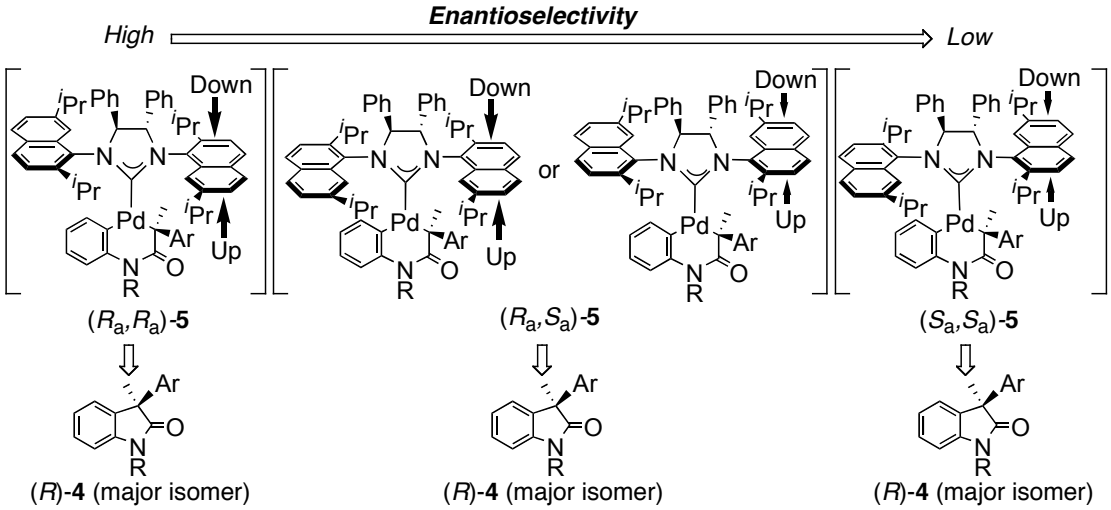
entry	R	Ar	cat.	% yield[a] and (% ee[b,c])		
				***R*$_a$,*R*$_a$**	***R*$_a$,*S*$_a$**	***S*$_a$,*S*$_a$**
7	Me	Ph	**2a**	98 (**86**)	98 (67)	98 (20)
8[d]	Me	Ph	**2b**	94 (67)	95 (52)	95 (34)
9[d]	Me	Ph	**2c**	98 (51)	98 (46)	--
10	Bn	Ph	**2a**	98 (**88**)	98 (45)	97 (50)
11	Bn	Ph	**2b**	89 (76)	96 (61)	--
12	Me	*p*-Tol	**2a**	99 (**87**)	98 (79)	97 (44)
13	Me	*p*-Tol	**2b**	98 (84)	98 (74)	--
14	Me	*p*-Tol	**2c**	98 (62)	98 (70)	--
15	Me	*o*-Tol	**2a**	99 (**85**)	97 (**89**)	98 (44)
16	Me	*m*-Tol	**2a**	99 (**80**)	96 (65)	98 (24)
17[d]	Me	*m*-Tol	**2b**	98 (71)	98 (49)	--
18	Me	1-Nap	**2a**	93 (**85**)	95 (80)	95 (34)
19[d]	Me	1-Nap	**2b**	92 (77)	95 (68)	--
20	Bn	1-Nap	**2a**	93 (**82**)	96 (66)	93 (49)

[a]Isolated yields. [b]Determined by chiral HPLC. [c]Absolute stereochemistry determined as (*R*)-configuration, see ref. 9d. [d]Reaction run at 50 °C.

Overall, results in table 2 validate the assumption made above that it is the chiral groups on the N-heterocycle that determine the absolute configuration of the carbon center in products **4a-g** (all *R*-configured). Finally, it should also be noted that adding up the results of entry 7 of Table 2 with (R_a,R_a)-**2a** (86% ee), (R_a,S_a)-**2a** (67% ee) and (S_a,S_a)-**2a** (20% ee) and taking into account the relative abundance of diastereomers in the NHC salt **1a** essentially replicates the *in situ* performance obtained in entry 2 of Table 1.

A viable model for the differences in selectivity between the three diastereomeric palladium complexes of **2a** is depicted in Scheme 1. The steric pressure exerted by the chiral NHC-phenyl groups onto the naphthyl side chains and subsequently onto the enantiodiscriminating side of the substrate would predominantly give intermediates **5** and, after reductive elimination, products with the observed (*R*)-configuration. Depending on the amount of steric pressure exerted onto

the naphthyl side chains, either higher or lower proportions of the depicted intermediate **5** would therefore be generated in the enantiodiscriminating carbon-metal bond-forming step preceding intermediate **5**. The higher steric pressure in the (R_a,R_a)-isomer means that the relative orientation of methyl *vs* aromatic group of the substrate as shown in (R_a,R_a)-**5**(*R*) is highly favored over (R_a,R_a)-**5**(*S*), while the (S_a,S_a)-isomer gives substantial amounts of (S_a,S_a)-**5**(*S*) and low enantiomeric excess of the (*R*)-**4** products. The lack of a plane of symmetry in (R_a,S_a)-**5**(*R*) means that two intermediates leading to the major isomer (*R*)-**4** may be operative, giving either high (left) or moderate (right) degrees of selectivity. In this case again, the model that we propose correctly reflects the observed experimental results that show an apparently random distribution of high and moderate selectivites when (R_a,S_a)-**2** are employed.



Scheme 1. Model explaining the differences in selectivity (derived from catalyst **2a**).

3.4 Conclusion

In conclusion, we report the synthesis of new NHC ligands with a chiral N-heterocycle and naphthyl side chains. Careful analysis of the imidazolinium salts showed the existence of three different isomers in such NHC structures. Pure palladium complexes incorporating these ligands were obtained after successful separation of their diastereomeric mixtures. The resulting compounds were tested in the asymmetric intramolecular α-arylation of amides and lead to the identification of a precatalyst [(R_a,R_a)-**2a**] that formed oxindoles in high yield and high enantiomeric purity. Analysis of the catalytic data demonstrates the dramatic effects on selectivity the orientation of the aromatic side chains can have in catalysis. In view of the

experimental results presented here, the assumption that (S_a,S_a)-isomers are responsible for enantioselectivity in this chiral NHC subclass should be questioned. Obviously, direct access to diastereomerically pure ligand precursors **1a-c** and its derivatives would provide an easier entry to their optimized use in catalysis and should also facilitate identification of even more effective and widely applicable ligand architectures. Studies with this aim are ongoing.

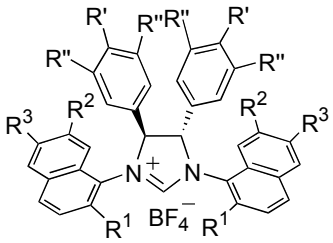
Acknowledgment. R.D. holds an Alfred Werner Assistant Professorship and thanks the foundation for generous financial support. X.L. thanks UZH (through a Drittmittelkredit) for support.

Supporting Information Available: Experimental procedures and CIFs for (R_a,R_a)-**2a** and (R_a,S_a)-**2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

3.5 Supplementary Data

In addition to the above results reported on the asymmetric intramolecular α-arylation of amides promoted by palladium complexes bearing NHC ligands **1a-d**, we also examined the catalytic performance of ligands **1e-h** in the same transformation. The variations of the ligands were carried out upon both the side chains and the *N*-heterocyclic backbone. Consequently, 2- and 7-positions of the naphthyl side chains were replaced with Me substituents to give **1e**, 2- and 6-positions of the naphthyl side chains were substituted with ^{i}Pr and Ad respectively to generate **1f**, and the phenyl groups on the backbone are replaced with other aromatic substituents (3,5-dimethylphenyl and *p*-methoxyphenyl) to give rise to ligands **1g** and **1h** (Figure 3). Following the previous synthetic procedure, ligands **1e-h** were prepared and ^{1}H NMR spectroscopy showed that these new NHC salts also exist as mixtures of three diastereomers.

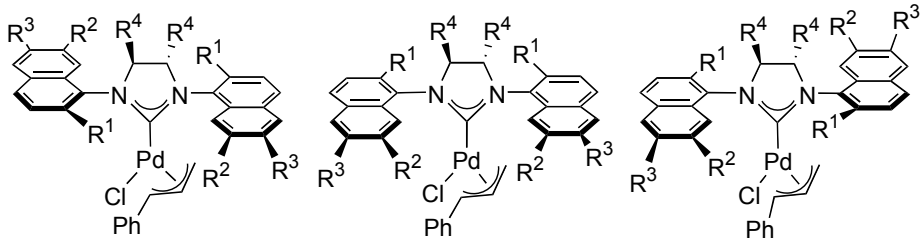
Subsequently, the NHC ligands **1e-h** were transferred onto palladium, again maintaining the diastereomeric ratio. These (NHC)Pd(cin)Cl complexes **2e-h** were then separated as diastereomerically pure compounds by flash chromatography (Figure 4). The absolute configuration of isomers of **2e** was assigned by X-ray diffraction studies (Figure 5), and the absolute configurations of isomers of **2f-h** were assigned by NMR spectroscopy.



mixture of three diastereomers

(*4S,5S*)-DiPhSIMeNap·HBF_4:
(**1e**, R^1 = R^2 = Me, R^3 = H, R' = R'' = H) [**27**(R_a,R_a):**64**(R_a,S_a):**9**(S_a,S_a)]
(*4S,5S*)-DiPhSIPrAd*Nap·HBF_4:
(**1f**, R^1 = ^{i}Pr, R^2 = H, R^3 = Ad, R' = R'' = H) [**31**(R_a,R_a):**54**(R_a,S_a):**15**(S_a,S_a)]
(*4S,5S*)-Di(3,5-DiMePh)SIPrNap·HBF_4:
(**1g**, R^1 = R^2 = ^{i}Pr, R^3 = H, R' = H, R'' = Me) [**65**(R_a,R_a):**27**(R_a,S_a):**8**(S_a,S_a)]
(*4S,5S*)-Di(*p*-MeOPh)SIPrNap·HBF_4:
(**1h**, R^1 = R^2 = ^{i}Pr, R^3 = H, R' = MeO, R'' = H) [**53**(R_a,R_a):**37**(R_a,S_a):**10**(S_a,S_a)]

Figure 3. New chiral *N*-Heterocyclic carbene precursors **1e-h**.



(R_a,R_a)-**2e** (21%)	(R_a,S_a)-**2e** (58%)	--
(R_a,R_a)-**2f** (28%)	(R_a,S_a)-**2f** (44%)	--
(R_a,R_a)-**2g** (59%)	(R_a,S_a)-**2g** (21%)	(S_a,S_a)-**2g** (5%)
(R_a,R_a)-**2h** (45%)	(R_a,S_a)-**2h** (31%)	--

Figure 4. Complexes **2e-h** (yields in brackets).

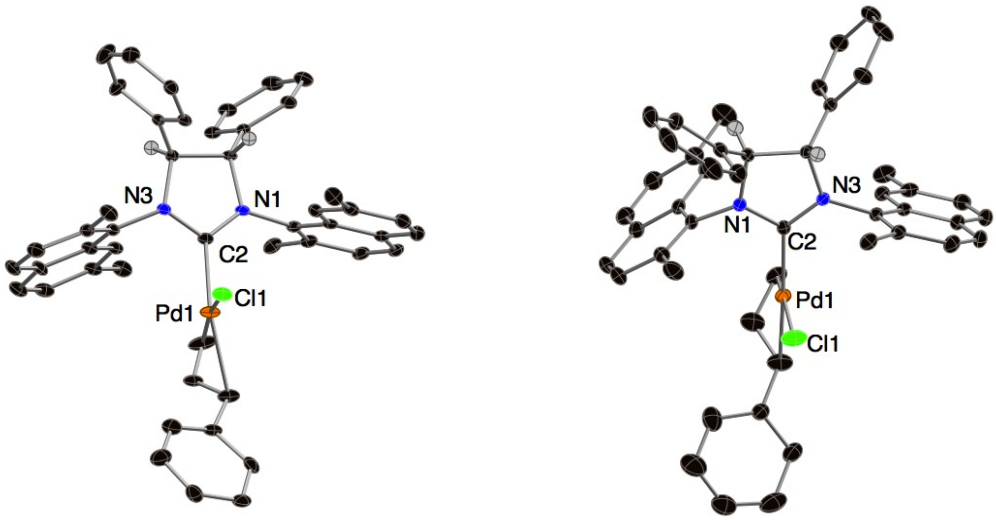
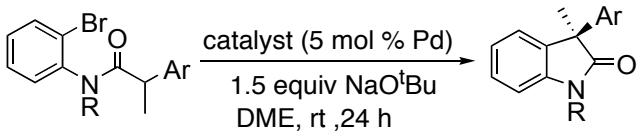


Figure 5. X-Rays of [(R_a,R_a)-(*4S,5S*)-DiPhSIMeNap]Pd(cin)Cl (below left, (R_a,R_a)-**2e**), and [(R_a,S_a)-(*4S,5S*)-DiPhSIMeNap]Pd(cin)Cl (below right, (R_a,S_a)-**2e**).

In order to evaluate the activity of these new palladium complexes, we subjected them to the asymmetric intramolecular α-arylation of amides to form oxindoles, and the catalytic results are summarized in Table 3.

Table 3. Asymmetric intramolecular α-arylation of amides with **2e-h**.



entry	R	Ar	cat.	% yield[a] and (% ee[b,c])	
				***R*$_a$,*R*$_a$**	***R*$_a$,*S*$_a$**
21	Me	Ph	**2e**	40 (16)	35 (3)
22	Me	Ph	**2f**	66 (79)	35 (61)
23	Me	Ph	**2g**	91 (**84**)	58 (76)
24	Me	Ph	**2h**	93 (82)	54 (73)
25	Bn	Ph	**2f**	91 (86)	--
26	Bn	Ph	**2g**	94 (**89**)	--
27	Bn	Ph	**2h**	93 (**89**)	--
28	Me	*p*-Tol	**2f**	79 (80)	--
29	Me	*p*-Tol	**2g**	98 (**90**)	--
30	Me	*p*-Tol	**2h**	96 (86)	--
31	Me	*m*-Tol	**2f**	94 (66)	--
32	Me	*m*-Tol	**2g**	98 (**79**)	--
33	Me	*m*-Tol	**2h**	93 (77)	--
34	Me	1-Nap	**2f**	72 (82)	--
35	Me	1-Nap	**2g**	92 (**86**)	--
36	Me	1-Nap	**2h**	64 (80)	--
37	Bn	1-Nap	**2f**	90 (81)	--
38	Bn	1-Nap	**2g**	92 (79)	--
39	Bn	1-Nap	**2h**	93 (**83**)	--

[a]Isolated yields. [b]Determined by chiral HPLC. [c]Absolute stereochemistry determined as (*R*)-configuration, see ref. 9d.

The results with **2e-h** for the model substrate (entries 21-24) revealed that bulkier ligands in the series are more efficient both in terms of reactivity and enantioselectivity, while catalyst **2e** bearing smaller ligand **1e** couldn't promote the transformation as well as others. Compared to catalyst *R*$_a$,*R*$_a$-**2a**, the enantioselectivity was slightly increased in several cases (entries 26, 27, 29, 35 and 39). The results with these modified ligand-metal precatalysts certainly show that better enantioselectivities can be reached when further fine-tuning is carried out.

We also investigated the catalytic behavior of one dimeric palladium complex bearing the NHC ligand of *R*$_a$,*R*$_a$-**1a**. Protonolysis of the cinnamyl ligand of *R*$_a$,*R*$_a$-**2a** with HCl in diethyl ether delivers [{$PdCl_2$(NHC)}$_2$] (**6**) in quantitative yield.[14] A

single-crystal X-ray diffraction study indicated the presence of two R_a,R_a-**1a** NHC ligands in the structure (Figure 6). Complex **6** was applied to the asymmetric synthesis of oxindole **3a**. The same ee was obtained as R_a,R_a-**2a**, albeit lower reactivity (rt, 48h, 39% yield, 86% ee).

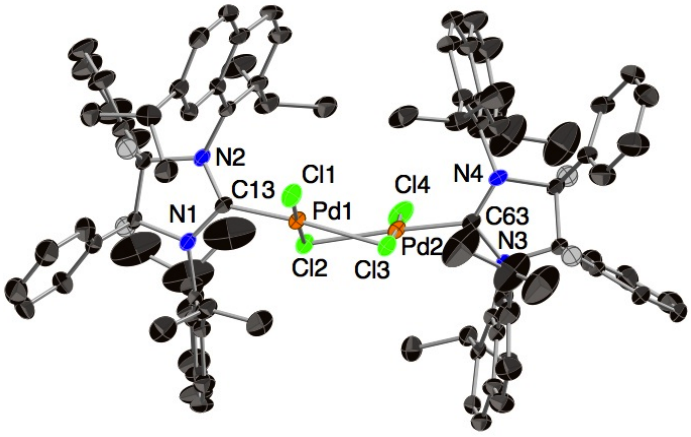


Figure 6. X-Ray of [{$PdCl_2$(R_a,R_a)-(*4S*,*5S*)-DiPhSIPrNap)}$_2$] (**6**).

3.6 Experimental Part

General Information. All reactions were carried out under a nitrogen atmosphere using Standard Schlenk-lines or gloveboxes (Mecaplex or Innovative Technology). All reagents were used as received unless otherwise noted. Solvents were purchased in the best quality available, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Solvents for NMR spectroscopy were degassed with nitrogen and dried over molecular sieves. NMR spectra were recorded on AV2 400 or AV2 500 MHz Bruker spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^{1}H and ^{13}C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). High-resolution electrospray ionization mass spectrometry was performed on a *Finnigan MAT 900* (*Thermo Finnigan*, San Jose, CA; USA) double-focusing magnetic sector mass spectrometer. 10 spectra were acquired. A mass accuracy ≤ 2 ppm was obtained in the peak matching acquisition mode by using a solution containing 2 µl PEG200, 2 µl PPG450, and 1.5 mg NaOAc (all obtained from Sigma-Aldrich, CH-Buchs) dissolved in 100ml MeOH (HPLC Supra grade, *Scharlau*, E-Barcelona) as internal standard.

GC-MS analysis was done on a Finnigan Voyager GC8000 Top. Elemental analyses were done on a Leco CHN-932 analyzer. Optical rotations were measured at 25 ºC on a Jasco P-2000 Polarimeter using a filtered Hg lamp (λ = 589 nm). X-ray crystallography was performed on a *Nonius Kappa CCD* area-detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. Compounds **3a-g** were prepared according to literature procedures.[9]

1*S*,2*S*-N,N′-Bis(2,7-diisopropylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine. A 250 mL schlenk flask was charged with $Pd(dba)_2$ (345 mg, 0.60 mmol), (±)-BINAP (448 mg, 0.72 mmol), NaO^tBu (1.73 g, 18.00 mmol) and toluene (180 mL) and stirred for 20 min. 1-Bromo-2,7-diisopropylnaphthalene (3.84 g, 13.20 mmol) and (*1S,2S*)-(-)-1,2-diphenylethylenediamine (1.27 g, 6.00 mmol) were then added and the solution was heated to 110 °C for 48 h. After cooling to room temperature, the resulting mixture was filtered through a celite filter and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by flash chromatography (SiO_2, 1:20 EtOAc/*n*-hexane) to afford 1*S*,2*S*-N,N′-bis(2,7-diisopropylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine as a white solid (2.13 g, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (s, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.27 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.88 (br s, 10H), 5.00 (br s, 2H), 4.96 (br s, 2H), 3.24 (sept, *J* = 6.9 Hz, 2H), 3.05 (sept, *J* = 6.9 Hz, 2H), 1.39 (d, *J* = 6.9 Hz, 6H), 1.30 (d, *J* = 6.9 Hz, 6H), 1.10 (d, *J* = 6.9 Hz, 6H), 0.49 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.21, 140.75, 139.78, 138.69, 132.19, 130.09, 128.70, 128.65, 128.08, 127.25, 125.13, 124.39, 123.53, 120.66, 34.95, 27.99, 24.78, 24.36, 22.77. HRMS (ESI) m/z calculated for $C_{46}H_{52}N_2Na$ $[M+Na]^+$ 655.4028, observed 655.4025.

***4S,5S-1*,3-Bis(2,7-diisopropylnaphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (DiPhSIPrNap·HBF$_4$) (1a).** Diamine 1*S*,2*S*-N,N′-bis(2,7-diisopropylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine (2.33 g, 3.69 mmol), ammonium tetrafluoroborate (464 mg, 4.43 mmol), triethyl orthoformate (6.14 mL, 36.90 mmol) and two drops formic acid were heated to 120 °C and stirred for 12 h. The resulting mixture was dried *in vacuo*, and the residue was purified by flash chromatography (SiO_2, 1:20 methanol:methylene chloride) to afford the product as an off-white foam (2.24 g, 83%). $[\alpha]^{25}_D$ = -174.2 (c = 1, CH_2Cl_2). ^{1}H NMR

($CDCl_3$, 400 MHz) exists as a mixture of three atropisomers (54:10:36): δ {8.92 (s, NC*H*N), 8.76 (s, NC*H*N), 8.69 (s, NC*H*N) (correspond to the three atropisomers of a single proton)}, 7.94-7.13 (m, Ar*H*) (correspond to the three atropisomers of twenty protons), {6.51 (d, *J* = 12.6 Hz, NC*H*Ph), 6.42 (s, NC*H*Ph), 6.20 (s, NC*H*Ph), 6.17 (d, *J* = 12.9 Hz, NC*H*Ph) (correspond to the three atropisomers of two protons)}, {3.71 (sept, *J* = 6.9 Hz, ArC*H*$(CH_3)_2$), 3.57 (sept, *J* = 6.9 Hz, ArC*H*$(CH_3)_2$), 3.39 (sept, *J* = 6.9 Hz, ArC*H*$(CH_3)_2$), 3.30 (sept, *J* = 6.9 Hz, ArC*H*$(CH_3)_2$), 3.08 (sept, *J* = 6.9 Hz, ArC*H*$(CH_3)_2$), 3.01-2.90 (m, ArC*H*$(CH_3)_2$) (correspond to the three atropisomers of four protons)}, {1.84 (d, *J* = 6.9 Hz, ArCH(C*H*$_3)_2$), 1.80 (d, *J* = 6.9 Hz, ArCH(C*H*$_3)_2$), 1.61 (d, *J* = 6.9 Hz, ArCH(C*H*$_3)_2$), 1.58 (d, *J* = 6.9 Hz, ArCH(C*H*$_3)_2$), 1.54 (d, *J* = 6.9 Hz, ArCH(C*H*$_3)_2$), 1.50 (d, *J* = 6.9 Hz, ArCH(C*H*$_3)_2$), 1.32-1.12 (m, ArCH(C*H*$_3)_2$), 0.59 (d, *J* = 6.9 Hz, ArCH(C*H*$_3)_2$), 0.51 (d, *J* = 6.9 Hz, ArCH(C*H*$_3)_2$) (correspond to the three atropisomers of twenty four protons)}. ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C NMR spectrum appeared complex): δ 159.35, 158.77, 158.63, 149.74, 149.59, 147.99, 147.94, 146.14, 146.05, 144.31, 143.84, 131.71, 131.62, 131.60, 131.58, 131.18, 131.11, 131.00, 130.86, 130.81, 130.51, 130.37, 130.34, 130.32, 130.29, 130.27, 130.07, 129.86, 129.82, 129.76, 129.73, 129.41, 129.39, 129.20, 129.16, 129.09, 128.95, 128.84, 128.79, 128.76, 128.34, 128.13, 127.92, 126.88, 126.39, 126.33, 125.52, 125.23, 125.02, 124.24, 123.95, 123.04, 122.98, 122.81, 118.63, 117.77, 116.78, 115.94, 75.21, 74.88, 73.35, 72.79, 35.30, 34.89, 34.86, 30.23, 30.20, 29.82, 29.62, 24.86, 24.79, 24.51, 24.46, 24.24, 24.17, 24.03, 23.83, 23.74, 23.67, 23.59, 22.23, 22.15, 21.79, 14.02. HRMS (ESI) m/z calculated for $C_{47}H_{51}N_2$ $[M\text{-}BF_4]^+$ 643.4052, observed 643.4057.

Chloro[(1,2,3-n)-3-phenyl-2-propenyl][*4S*,*5S*-*1*,3-Bis(2,7-diisopropylnaphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-imidazol-2-ylidene] palladium(II) [(DiPhSIPrNap)Pd(cinnamyl)Cl] (**2a**): DiPhSIPrNap·HBF_4 (1.02 g, 1.40 mmol), KO^{t}Bu (157 mg, 1.40 mmol) and $[Pd(cinnamyl)Cl]_2$ (344 mg, 0.66 mmol) were mixed together in a round flask in the glovebox. Dry THF (60 mL) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo*, and the residue was separated by flash chromatography (SiO_2, 1:8→1:3 EtOAc/*n*-hexane) to afford three atropisomers (1.08 g, 89.4%). Elemental analysis (%) calculated for $C_{56}H_{59}PdN_2Cl$•$0.5CH_2Cl_2$: C, 71.85; H, 6.40; N, 2.97. Found: C, 72.06;

H, 6.40; N, 2.97. HRMS (ESI) m/z calculated for $^{12}C_{56}H_{59}{}^{104}Pd^{14}N_2{}^{35}ClNa$ $[M+Na]^+$ 921.3304, observed 921.3290.

Data for ***S*$_a$,*S*$_a$-2a** are as follows (first point). (90 mg, 7.4%). $[\alpha]^{25}_D$ = +35.8 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (s, 2H), 7.76-7.74 (br m, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.30 (br s, 4H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.03-6.93 (br m, 9H), 6.60-6.55 (br m, 2H), 5.85 (br s, 1H), 5.81 (br s, 1H), 4.54-4.47 (br m, 0.54H), 4.01-3.80 (br m, 3.36H), 3.28-2.98 (br m, 3.10H), 1.87-1.25 (m, 25H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.77, 145.56, 144.16, 138.79, 136.27, 133.01, 132.51, 131.70, 129.36, 128.97, 128.86, 128.67, 128.10, 127.60, 127.33, 126.33, 125.30, 123.84, 123.41, 109.73, 48.97, 34.80, 29.54, 25.80, 24.97, 24.11, 23.44.

Data for ***R*$_a$,*R*$_a$-2a** are as follows (second point). (593 mg, 49.3%). $[\alpha]^{25}_D$ = -439.9 (c = 1, CH_2Cl_2). Crystals suitable for diffraction studies were grown from a diethyl ether/n-hexane solution of ***R*$_a$,*R*$_a$-2a**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (br s, 2H), 7.84-7.59 (br m, 4H), 7.47-6.80 (br m, 19H), 6.04 (br s, 2H), 5.10-5.04 (m, 0.68H), 4.44-4.42 (br m, 0.32H), 4.18 (d, *J* = 12 Hz, 0.68H), 4.11 (d, *J* = 12 Hz, 0.32H), 3.52-2.49 (br m, 2H), 3.31 (sept, *J* = 6.9 Hz, 2H), 2.62 (d, *J* = 4 Hz, 0.68H), 2.19 (d, *J* = 4 Hz, 0.32H), 2.00 (d, *J* = 12 Hz, 0.32H), 1.63-1.18 (m, 18H), 0.50 (d, *J* = 12 Hz, 0.68H), 0.46-0.25 (br m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.60, 147.05, 137.44, 131.92, 130.86, 129.25, 129.15, 128.98, 128.56, 128.19, 127.97, 127.56, 127.25, 125.82, 108.97, 106.25, 92.63, 90.86, 89.52, 47.62, 46.57, 35.34, 34.33, 28.81, 28.56, 26.67, 26.24, 24.80, 23.99, 23.85, 23.37, 22.55, 15.49, 14.27.

Data for ***R*$_a$,*S*$_a$-2a** are as follows (third point). (392 mg, 32.6%). $[\alpha]^{25}_D$ = -309.5 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (s, 1H), 8.01-7.44 (br m, 9H), 7.30-7.22 (br m, 8H), 7.09-6.84 (br m, 6H), 6.57 (br s, 1H), 6.06-6.01 (br m, 1H), 5.81-5.79 (br m, 1H), 4.48 (br s, 0.5H), 4.28 (br s, 0.5H), 3.96-3.81 (br m, 2H), 3.59-3.41 (br m, 2H), 3.06 (br s, 1H), 2.91 (br s, 0.5H), 2.69 (br s, 0.5H), 1.78-1.15 (br m, 21H), 0.35-0.18 (br m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.74, 212.45, 212.13, 193.88, 163.99, 152.96, 148.35, 148.22, 148.09, 147.82, 147.43, 147.22, 145.22, 144.97, 144.47, 138.29, 137.79, 137.63, 137.10, 136.49, 132.22, 132.03, 131.92, 131.76, 131.46, 130.51, 129.92, 129.61, 129.47, 129.33, 129.18, 129.14, 129.02, 128.96, 128.81, 128.68, 128.62, 128.48, 128.30, 128.15, 128.04, 127.41, 127.23, 126.36, 125.80, 125.73, 124.83, 124.62, 124.34, 124.11, 123.92, 123.07, 122.71, 121.07, 120.83, 119.78, 109.96, 190.10, 105.92, 89.33, 89.08, 87.55, 77.44,

76.50, 75.93, 75.78, 66.03, 53.00, 49.48, 48.64, 35.88, 35.27, 34.77, 34.31, 32.12, 30.15, 29.98, 29.89, 29.63, 29.55, 29.00, 28.67, 28.54, 26.54, 26.02, 25.48, 25.32, 25.22, 24.79, 24.66, 24.58, 24.50, 24.30, 24.23, 24.03, 23.93, 23.93, 23.74, 23.54, 23.47, 23.53, 23.47, 22.88, 22.52, 15.47, 14.25.

1*S*,2*S*-N,N′-Bis(2-isopropylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine. A 250 mL schlenk flask was charged with $Pd(dba)_2$ (345 mg, 0.60 mmol), (±)-BINAP (448 mg, 0.72 mmol), NaO^tBu (1.73 g, 18.00 mmol) and toluene (180 mL) and stirred for 20 min. 1-Bromo-2-isopropylnaphthalene (3.29 g, 13.20 mmol) and (*1S,2S*)-(-)-1,2-diphenylethylenediamine (1.27 g, 6.00 mmol) were then added and the solution was heated to 110 °C for 48 h. After cooling to room temperature, the resulting mixture was filtered through a celite and silica gel filter and washed with CH_2Cl_2. The filtrate was concentrated, and the residue was dissolved in hexane and filtered through a celite filter. The filtrate was concentrated and the residue was purified by flash chromatography (SiO_2, 1:3 CH_2Cl_2/hexane) to afford 1*S*,2*S*-N,N′-bis(2-isopropylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine as a white solid (2.04 g, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.44-7.32 (m, , 4H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.99-6.92 (m, 10H), 5.03 (d, *J* = 4.3 Hz, 2H), 4.81 (br s, 2H), 3.22 (sept, *J* = 6.9 Hz, 2H), 1.07 (d, *J* = 6.9 Hz, 6H), 0.73 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.50, 139.05, 138.81, 133.49, 129.93, 128.66, 128.53, 128.07, 127.31, 125.49, 125.01, 124.37, 124.26, 124.24, 69.05, 28.02, 24.42, 22.85. HRMS (ESI) m/z calculated for $C_{40}H_{40}N_2Na$ $[M+Na]^+$ 571.3089, observed 571.3084.

***4S,5S-1*,3-Bis(2-diisopropylnaphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (DiPhSI2PrNap·HBF$_4$) (1b).** Diamine 1*S*,2*S*-N,N′-bis(2-isopropylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine (1.40 g, 2.55 mmol), ammonium tetrafluoroborate (321 mg, 3.06 mmol), triethyl orthoformate (4.25 mL, 25.50 mmol) and two drops formic acid were heated to 120 °C and stirred for 12 h. The resulting mixture was dried *in vacuo*, and the residue was purified by flash chromatography (SiO_2, 1:20 methanol:methylene chloride) to afford the product as an off-white foam (1.52 g, 92%). $[\alpha]^{25}_D$ = -195.7 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) exists as a mixture of three atropisomers (8:41:51): δ {8.71 (s, NC*H*N), 8.67 (s, NC*H*N), 8.60 (s, NC*H*N) (correspond to the three atropisomers of a single proton)}, 8.39-7.18 (m, Ar*H*) (correspond to the three atropisomers of twenty

two protons), {6.62 (d, *J* = 13.2 Hz, NC*H*Ph), 6.59 (s, NC*H*Ph), 6.22 (s, NC*H*Ph), 6.18 (d, *J* = 13.2 Hz, NC*H*Ph) (correspond to the three atropisomers of two protons)}, {3.76 (sept, *J* = 6.9 Hz, ArC*H*(CH_3)$_2$), 3.59 (sept, *J* = 6.9 Hz, ArC*H*(CH_3)$_2$), 3.29-3.05 (m, ArC*H*(CH_3)$_2$) (correspond to the three atropisomers of two protons)}, {1.77 (d, *J* = 6.9 Hz, ArCH(C*H*$_3$)$_2$), 1.69 (d, *J* = 6.9 Hz, ArCH(C*H*$_3$)$_2$), 1.62-1.53 (m, ArCH(C*H*$_3$)$_2$), 1.31-1.08 (m, ArCH(C*H*$_3$)$_2$), 0.72 (d, *J* = 6.9 Hz, ArCH(C*H*$_3$)$_2$), 0.66 (d, *J* = 6.9 Hz, ArCH(C*H*$_3$)$_2$), (correspond to the three atropisomers of twelve protons)}. ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C NMR spectrum appeared complex): δ 162.02, 158.72, 158.51, 146.62, 145.86, 144.08, 132.95, 132.82, 132.49, 132.17, 132.05, 132.01, 131.01, 130.98, 130.93, 130.36, 130.05, 129.84, 129.83, 129.67, 129.57, 129.52, 129.42, 129.35, 129.29, 129.27, 129.14, 129.07, 128.57, 127.88, 127.23, 127.12, 126.88, 125.74, 124.77, 124.64, 123.90, 123.62, 123.59, 122.51, 121.29, 120.40, 75.66, 74.12, 73.58, 41.88, 36.50, 30.37, 29.84, 29.77, 25.22, 25.07, 24.60, 24.11, 22.41, 21.98, 14.83, 12.70. HRMS (ESI) m/z calculated for $C_{41}H_{39}N_2$ $[M\text{-}BF_4]^+$ 559.3113, observed 559.3111.

Chloro[(1,2,3-n)-3-phenyl-2-propenyl][*4S*,*5S*-*1*,3-Bis(2-diisopropylnaphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-imidazol-2-ylidene] palladium(II) [(DiPhSI2PrNap)Pd(cinnamyl)Cl] (**2b**): DiPhSI2PrNap·HBF_4 (1.20 g, 1.86 mmol), KO^{t}Bu (209 mg, 1.86 mmol) and [Pd(cinnamyl)Cl]$_2$ (458 mg, 0.88 mmol) were mixed together in a round flask in the glovebox. Dry THF (70 mL) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo, and the residue was separated by flash chromatography (SiO_2, 1:5→1:3 EtOAc/hexane) to afford three atropisomers (1.25 g, 86%). Elemental analysis (%) calculated for $C_{50}H_{47}PdN_2Cl$•$0.5C_6H_{14}$: C, 73.94; H, 6.32; N, 3.25. Found: C, 74.24; H, 6.49; N, 3.26. HRMS (ESI) m/z calculated for $^{12}C_{50}H_{47}{}^{104}Pd^{14}N_2$ $[M\text{-}Cl]^+$ 779.2779, observed 779.2776.

Data for ***R*$_a$,*S*$_a$-2b** are as follows (first point). (547 mg, 37.7%). $[\alpha]^{25}_D$ = -291.9 (c = 1, CH_2Cl_2). Crystals suitable for diffraction studies were grown from a EtOAc/n-hexane solution of ***R*$_a$,*S*$_a$-2b**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.49-8.44 (m, 2H), 7.96-7.29 (br m, 17H), 7.09-6.86 (br m, 7H), 6.58 (br s, 1H), 6.19-6.19 (br m, 1H), 5.72 (br s, 1H), 4.40-3.66 (br m, 4H), 2.78 (br s, 0.5H), 2.48 (br s, 0.5 H), 1.81-0.74 (m, 10H), 0.39 (br s, 1.5H), 0.22 (br s, 1.5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 216.59, 214.91, 171.26, 148.15, 147.97, 147.79, 144.50, 144.30, 138.43, 138.23,

137.62, 137.47, 136.82, 136.70, 136.50, 133.10, 133.03, 132.36, 131.89, 131.75, 130.83, 130.70, 129.35, 129.24, 129.16, 128.87, 128.74, 128.08, 128.03, 127.98, 127.82, 127.70, 127.60, 127.41, 127.25, 127.14, 126.73, 126.33, 125.58, 125.45, 125.26, 125.11, 124.62, 123.63, 123.37, 110.42, 109.12, 106.15, 88.56, 88.47, 87.20, 78.05, 60.53, 50.3, 49.74, 30.02, 29.86, 28.71, 28.60, 26.23, 25.59, 24.99, 24.84, 24.64, 24.53, 24.35, 23.88, 23.7321.20, 14.37.

Data for ***S*$_a$,*S*$_a$-2b** are as follows (second point). (10 mg, 0.7%). $[\alpha]^{25}_D$ = -24.5 (c = 0.25, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (br d, *J* = 7.1 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.65 (br s, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.35-7.6.92 (br m, 17H), 7.51-6.44 (m, 2H), 5.74 (br d, *J* = 14.3 Hz, 2H), 4.22-3.70 (br m, 5H), 3.18 (br d, *J* = 5.8 Hz, 0.5H), 2.90 (br d, *J* = 5.2 Hz, 0.5H), 1.74-1.24 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.63, 143.36, 137.48, 137.02, 132.87, 131.89, 129.49, 129.01, 128.83, 128.58, 128.47, 128.30, 127.97, 127.48, 127.41, 127.01, 126.39, 125.68, 124.46, 110.29, 110.01, 88.06, 53.63, 49.93, 29.92, 29.65, 25.13, 24.44.

Data for ***R*$_a$,*R*$_a$-2b** are as follows (third point). (697 mg, 48.1%). $[\alpha]^{25}_D$ = -351.3 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.49 (br s, 2H), 7.89-7.75 (br m, 6H), 7.57 (br s, 2H), 7.51-6.76 (br m, 17H), 6.06 (br s, 2H), 5.08-5.00 (m, 0.68H), 4.53-4.44 (br m, 0.32H), 4.20 (d, *J* = 12 Hz, 0.68H), 4.10 (d, *J* = 12 Hz, 0.32H), 3.66-3.34 (br m, 2H), 2.54 (d, *J* = 4 Hz, 0.68H), 1.97 (d, *J* = 4 Hz, 0.32H), 1.79-1.17 (m, 7H), 0.94-0.26 (br m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.23, 137.52, 133.20, 130.77, 129.44, 129.24, 129.11, 129.03, 128.39, 128.10, 127.58, 127.33, 126.84, 126.66, 125.71, 109.33, 108.97, 92.02, 74.84, 47.11, 29.74, 25.76, 23.39.

2-Cyclohexylnaphthalene. In a 50 mL 3-necked flask, equipped with a condenser, an addition funnel and a N_2 inlet, were added 592 mg of magnesium turnings (and 1 crystal of I_2) under N_2 flow. In the addition funnel was charged 4.80 g of 2-bromonaphthalene and 25 mL THF. 5 mL of this solution was added into the flask and warmed with the heating gun for 1 min and the solution became light brown. The flask was then warmed with an oil bath at 60°C and the remaining solution was added dropwise. At the end of the addition, the mixture was reflux for 1h. In a 250 mL schlenk flask was added 3.78 g of 1-bromocyclohexane and 390 mg of $(FeCl_3)_2(TMEDA)_3$ in 20 mL THF. The grignard reagent was then added dropwise into the schlenk flask and stirred at room temperature for 2h. The reaction was quenched with 1 N HCl aqueous solution, and extracted with Et_2O. The product was

isolated as a colorless oil by flash chromatography using n-hexane as eluent (4.10 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.85 (m, 3H), 7.73 (s, 1H), 7.58-7.45 (m, 3H), 2.80-2.72 (m, 1H), 2.09-1.88 (m, 5H), 1.68-1.39 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.73, 133.92, 132.35, 127.92, 127.80, 127.75, 126.38, 125.94, 125.20, 124.73, 44.88, 34.63, 27.16, 26.45. HRMS (EI) m/z calculated for $C_{16}H_{18}$ $[M]^+$ 210.1409, observed 210.1406.

1-Bromo-2-cyclohexylnaphthalene. 2.63 g 2-cyclohexylnaphthalene were dissolved in 50 mL CH_2Cl_2, and then a 50 mL CH_2Cl_2 solution of Br_2 (1.0 eq.) was added dropwise over 1h at 0°C. After 3h the reaction was finished (confirmed by GC-MS). The reaction was quenched by adding 100 mL of a 25% $Na_2S_2O_3$ aqueous solution. The CH_2Cl_2 phase was separated and washed with 200 mL water, 200 mL 5% Na_2CO_3, dried by $MgSO_4$, filtered and concentrated under vacuum to afford a light yellow oil (3.25 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33 (d, *J* = 6.8 Hz, 1H), 7.78-7.71 (m, 2H), 7.58-7.34 (m, 3H), 3.47-3.33 (m, 1H), 2.72-1.78 (m, 5H), 1.56-1.24 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.45, 133.47, 132.81, 128.13, 127.97, 127.93, 127.39, 125.97, 125.18, 123.65, 44.64, 33.39, 27.09, 26.47. HRMS (EI) m/z calculated for $C_{16}H_{17}Br$ $[M]^+$ 288.0514, observed 288.0514.

1*S*,2*S*-N,N′-Bis(2-cyclohexylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine. A 250 mL schlenk flask was charged with $Pd(dba)_2$ (282 mg, 0.49 mmol), (±)-BINAP (367 mg, 0.59 mmol), NaO^tBu (1.42 g, 14.76 mmol) and toluene (170 mL) and stirred for 20 min. 1-Bromo-2-cyclohexylnaphthalene (3.13 g, 10.82 mmol) and (*1S,2S*)-(-)-1,2-diphenylethylenediamine (1.04 g, 4.92 mmol) were then added and the solution was heated to 110 °C for 16 h. After cooling to room temperature, the resulting mixture was filtered through a celite filter and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by flash chromatography (SiO_2, 1:20 EtOAc/*n*-hexane) to afford 1*S*,2*S*-N,N′-bis(2-cyclohexylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine as a white solid (1.46 g, 47%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.61 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 7.0 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.46-4.39 (m, 4H), 7.30 (d, *J* = 8.6, 2H), 7.01-6.96 (m, 10H), 5.03 (br s, 2H), 4.94 (br s, 2H), 2.98-2.94 (m, 2H), 1.92-1.11 (m, 20H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.51, 139.40, 138.18, 133.41, 130.22, 128.60, 128.38, 128.13, 127.24, 125.40, 125.13, 124.98, 124.45, 124.23, 69.25, 38.86, 34.95, 33.26, 31.81, 27.60, 27.19,

26.46, 22.87, 14.34. HRMS (ESI) m/z calculated for $C_{46}H_{48}N_2Na$ $[M+Na]^+$ 651.3715, observed 651.3723.

***4S*,*5S*-*1*,3-Bis(2-cyclohexylnaphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (DiPhSI2CyNap·HBF$_4$) (1c).** Diamine 1*S*,2*S*-N,N′-bis(2-cyclohexylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine (1.46 g, 2.32 mmol), ammonium tetrafluoroborate (292 mg, 2.79 mmol), triethyl orthoformate (3.86 mL, 23.20 mmol) and two drops formic acid were heated to 120 °C and stirred for 16 h. The resulting mixture was dried *in vacuo*, and the residue was purified by flash chromatography (SiO_2, 1:20 methanol:methylene chloride) to afford the product as an off-white foam (1.57 g, 93%). $[\alpha]^{25}_D$ = -230.9 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) exists as a mixture of three atropisomers (71:21:8): δ {8.99 (s, NC*H*N), 8.73 (s, NC*H*N), 8.55 (s, NC*H*N) (correspond to the three atropisomers of a single proton)}, 8.34-7.22 (m, Ar*H*) (correspond to the three atropisomers of twenty two protons), {6.61 (s, NC*H*Ph), 6.43 (d, *J* = 11.4 Hz, NC*H*Ph), 6.28 (d, *J* = 11.4 Hz, NC*H*Ph), 6.03 (s, NC*H*Ph) (correspond to the three atropisomers of two protons)}, {3.32-3.22 (m, *Cy*), 2.75-2.56 (m, *Cy*), 2.33-1.17 (m, *Cy*), 0.28-0.26 (m, *Cy*) (correspond to the three atropisomers of twenty two protons)}. ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C NMR spectrum appeared complex): δ 159.89, 158.85, 158.80, 145.56, 144.93, 142.97, 142.58, 133.21, 132.75, 132.13, 132.03, 131.85, 131.26, 131.17, 130.40, 129.97, 129.95, 129.78, 129.74, 129.67, 129.62, 129.33, 129.05, 128.95, 128.88, 128.41, 128.31, 127.29, 127.19, 127.00, 126.71, 124.93, 124.86, 124.81, 124.64, 121.75, 120.86, 120.20, 76.54, 76.22, 74.54, 73.20, 66.01, 41.48, 40.80, 40.64, 35.42, 35.03, 34.63, 34.57, 34.22, 32.67, 31.86, 31.06, 27.62, 27.51, 27.19, 26.98, 26.72, 26.12, 25.96, 25.82, 22.51, 15.44, 14.23. HRMS (ESI) m/z calculated for $C_{47}H_{47}N_2$ $[M-BF_4]^+$ 639.3739, observed 639.3741.

Chloro[(1,2,3-n)-3-phenyl-2-propenyl][*4S*,*5S*-*1*,3-Bis(2-cyclohexylnaphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-imidazol-2-ylidene] palladium(II) [(DiPhSI2CyNap)Pd(cinnamyl)Cl] (2c): DiPhSI2CyNap·HBF_4 (1.03 g, 1.42 mmol), KO^{t}Bu (159 mg, 1.42 mmol) and $[Pd(cinnamyl)Cl]_2$ (352 mg, 0.68 mmol) were mixed together in a round flask in the glovebox. Dry THF (60 mL) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo, and the residue was separated by flash chromatography (SiO_2, 1:5→1:3 EtOAc/*n*-

hexane) to afford two pure atropisomers (753 mg, 62%) (*One of the three atropisomers couldn't be isolated as a pure isomer*). Elemental analysis (%) calculated for $C_{56}H_{55}PdN_2Cl•1.5CH_2Cl_2$: C, 67.36; H, 5.70; N, 2.73. Found: C, 67.56; H, 5.73; N, 2.62. HRMS (ESI) m/z calculated for $^{12}C_{56}H_{55}{}^{104}Pd^{14}N_2$ $[M\text{-}Cl]^+$ 859.3405, observed 859.3397.

Data for ***R*$_a$,*S*$_a$-2c** are as follows (first point). (164 mg, 14%). $[\alpha]^{25}_D$ = -274.8 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (d, *J* = 8.2Hz, 2H), 7.97-6.65 (m, 25H), 6.13-6.07 (m, 1H), 5.79 (d, *J* = 9.3Hz, 0.38H), 5.67 (d, *J* = 9.3Hz, 0.62H), 4.56-2.52 (m, 6H), 2.17-0.76 (m, 19H), (-0.01)-(-0.18) (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 216.07, 214.01, 171.19, 163.79, 146.87, 143.15, 138.17, 138.13, 137.78, 137.62, 137.50, 137.14, 137.04, 136.50, 133.01, 132.51, 132.37, 131.84, 131.71, 130.72, 130.67, 129.37, 129.20, 129.14, 129.01, 128.90, 128.78, 128.67, 128.02, 127.96, 127.83, 127.55, 127.24, 127.06, 126.64, 126.32, 126.26, 126.18, 126.04, 125.62, 125.49, 125.05, 124.95, 123.52, 109.86, 108.89, 106.16, 86.77, 78.59, 77.78, 76.66, 60.48, 50.73, 40.88, 39.13, 38.79, 35.16, 34.97, 33.82, 33.67, 33.59, 31.70, 27.60, 27.57, 27.29, 26.91, 26.83, 26.76, 26.40, 26.35, 26.27, 22.77, 22.45, 14.33, 14.26, 14.20.

Data for ***R*$_a$,*R*$_a$-2c** are as follows (third point). (589 mg, 48%). $[\alpha]^{25}_D$ = -292.5 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.58 (br s, 2H), 7.87-7.03 (br m, 25H), 6.04 (br s, 2H), 5.00 (br s, 0.5H), 4.45-4.23 (m, 1.6H), 3.04-2.87 (br m, 2.4H), 2.60 (br s, 1H), 1.87-1.07 (m, 18H), 0.37 (d, *J* = 8Hz, 0.5H), (-0.06)-(-0.30) (br m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.80, 171.29, 137.71, 137.36, 133.20, 130.87, 129.24, 129.14, 129.04, 128.95, 128.31, 128.11, 127.93, 127.35, 126.77, 126.54, 125.67, 109.05, 108.37, 92.22, 89.89, 88.79, 75.18, 60.55, 53.64, 48.20, 46.30, 39.43, 35.19, 34.30, 33.22, 27.35, 27.04, 26.37, 22.51, 14.38, 14.24.

1*R*,2*R*-N,N′-Bis(2,7-diisopropylnaphthalen-1-yl)-1,2-diaminocyclohexane. A 250 mL schlenk flask was charged with $Pd(dba)_2$ (173 mg, 0.30 mmol), (±)-BINAP (187 mg, 0.30 mmol), NaO^tBu (865 mg, 9.00 mmol) and toluene (90 mL) and stirred for 20 min. 1-Bromo-2,7-diisopropylnaphthalene (1.92 g, 6.60 mmol) and (1*R*,2*R*)-(-)-1,2-diaminocyclohexane (343 mg, 3.00 mmol) were then added and the solution was heated to 90 °C for 48 h. After cooling to room temperature, the resulting mixture was filtered through a celite filter and washed by CH_2Cl_2. The filtrate was concentrated and the residue was purified by flash chromatography (SiO_2, 1:40 EtOAc/*n*-hexane)

to afford 1*R*,2*R*-N,N′-bis(2,7-diisopropylnaphthalen-1-yl)-1,2-diaminocyclohexane as a white solid (1.18 g, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (s, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.34 (dd, *J* = 8.4, 1.6 Hz, 2H), 4.44 (br s, 2H), 3.80 (sept, *J* = 6.9 Hz, 2H), 4.96 (br d, *J* = 7.4 Hz, 2H), 3.11 (sept, *J* = 6.9 Hz, 2H), 1.81 (br d, *J* = 13.3 Hz, 2H), 1.57-1.54 (br m, 2H), 1.43-1.30 (m, 26H), 1.05-1.03 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.98, 139.85, 139.03, 132.05, 128.33, 125.17, 124.16, 123.46, 121.10, 64.54, 34.83, 33.12, 27.93, 25.26, 24.81, 24.51, 24.41, 23.53. HRMS (ESI) m/z calculated for $C_{38}H_{50}N_2Na$ $[M+Na]^+$ 557.3872, observed 557.3864.

***4R*,*5R*-*1*,3-Bis(2,7-diisopropylnaphthalen-1-yl)-octahydro-1*H*-benzoimidazol-3-ium tetrafluoroborate (CySIPrNap·HBF$_4$) (1d).** Diamine 1*R*,2*R*-N,N′-bis(2,7-diisopropylnaphthalen-1-yl)-1,2-diaminocyclohexane (869 mg, 1.62 mmol), ammonium tetrafluoroborate (170 mg, 1.62 mmol), triethyl orthoformate (2.70 mL, 16.20 mmol) and two drops formic acid were heated to 120 °C and stirred for 14 h. The resulting mixture was dried *in vacuo*, and the residue was purified by flash chromatography (SiO_2, 1:20 methanol:methylene chloride) to afford the product as an off-white foam (870 mg, 85%). $[\alpha]^{25}_{D}$ = -132.3 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) exists as a mixture of three atropisomers (40:15:45): δ {8.36 (s, NC*H*N), 8.33 (s, NC*H*N), 8.26 (s, NC*H*N) (correspond to the three atropisomers of a single proton)}, 7.97-7.37 (m, Ar*H*) (correspond to the three atropisomers of ten protons), {4.72-4.50 (m, NC*H*Ph) (correspond to the three atropisomers of two protons)}, {3.74 (sept, *J* = 6.9 Hz, ArC*H*$(CH_3)_2$), 3.66 (sept, *J* = 6.9 Hz, ArC*H*$(CH_3)_2$), 3.30-3.18 (m, ArC*H*$(CH_3)_2$), 3.15 (sept, *J* = 6.9 Hz, ArC*H*$(CH_3)_2$) (correspond to the three atropisomers of four protons)}, {1.98-1.92 (m, 6H), 1.55-1.31 (m, 26H) (correspond to the three atropisomers of thirty two protons)}. ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C NMR spectrum appeared complex): δ 161.93, 161.49, 161.22, 150.56, 149.93,149.84, 149.52, 146.84, 146.09,144.81, 144.17, 131.96, 131.93, 131.72, 131.65, 131.63, 131.11, 130.86, 129.88, 129.75, 129.65, 129.51, 129.10, 128.81, 127.13, 126.49, 126.25, 126.21, 125.70, 125.47, 124.89, 124.76, 123.79, 123.60, 123.34, 123.24, 118.57, 118.06, 117.21, 116.95, 73.68, 73.65, 72.92, 72.64, 35.24, 35.21, 35.12, 34.57, 29.85, 29.80, 29.76, 29.56, 28.64, 27.92, 27.79, 27.16, 25.43, 25.17, 24.92, 24.59, 24.38, 24.32, 24.31, 24.14, 24.02, 23.94,

23.86, 23.75, 23.56, 23.15, 22.79. HRMS (ESI) m/z calculated for $C_{39}H_{49}N_2$ $[M\text{-}BF_4]^+$ 545.3896, observed 545.3896.

1*S*,2*S*-N,N′-Bis(2,7-dimethylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine. A 250 mL schlenk flask was charged with $Pd(dba)_2$ (230 mg, 0.40 mmol), (±)-BINAP (299 mg, 0.48 mmol), NaO^tBu (1.15 g, 12.00 mmol) and toluene (120 mL) and stirred for 20 min. 1-Bromo-2,7-dimethylnaphthalene (1.98 g, 8.40 mmol) and (*1S,2S*)-(-)-1,2-diphenylethylenediamine (0.85 g, 4.00 mmol) were then added and the solution was heated to 110 °C for 16 h. After cooling to room temperature, the resulting mixture was filtered through a celite filter and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by flash chromatography (SiO_2, 1:4 CH_2Cl_2/*n*-hexane) to afford 1*S*,2*S*-N,N′-bis(2,7-dimethylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine as a white solid (1.90 g, 91%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.01 (s, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.08-7.01 (m, 12H), 5.05 (br s, 2H), 4.66 (br s, 2H), 2.40 (s, 6H), 2.12 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.07, 140.54, 134.90, 132.06, 129.09, 128.74, 128.41, 128.06, 127.44, 127.04, 126.57, 122.59, 122.53, 68.09, 22.26, 19.12. HRMS (ESI) m/z calculated for $C_{38}H_{36}N_2Na$ $[M+Na]^+$ 543.2771, observed 543.2767.

***4S,5S-1*,3-Bis(2,7-dimethylnaphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (DiPhSIMeNap·HBF$_4$) (1e).** Diamine 1*S*,2*S*-N,N′-bis(2,7-dimethylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine (1.87 g, 3.60 mmol), ammonium tetrafluoroborate (453 mg, 4.32 mmol), triethyl orthoformate (6.00 mL, 36.00 mmol) and two drops formic acid were heated to 110 °C and stirred for 12 h. The resulting mixture was dried *in vacuo*, and the residue was purified by flash chromatography (SiO_2, 1:20 MeOH:CH_2Cl_2) to afford the product as an off-white foam (2.15 g, 97%). $[\alpha]^{27}_D$ = -336.81 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz) exists as a mixture of three atropisomers (27:64:9): δ {9.13 (s, NC*H*N), 8.90 (s, NC*H*N), 8.54 (s, NC*H*N) (correspond to the three atropisomers of a single proton)}, 7.96-7.14 (m, Ar*H*) (correspond to the three atropisomers of twenty protons), {6.34 (d, *J* = 12.8 Hz, NC*H*Ph), 6.32 (s, NC*H*Ph), 6.28 (s, NC*H*Ph), 6.20 (d, *J* = 11.7 Hz, NC*H*Ph) (correspond to the three atropisomers of two protons)}, {3.04 (s, ArCH_3), 2.99 (s, ArCH_3), 2.85 (s, ArCH_3), 2.75 (s, ArCH_3), 2.48 (s, ArCH_3), 2.43 (s, ArCH_3), 2.17 (s, ArCH_3), 2.16 (s, ArCH_3), (correspond to the three atropisomers of twenty four protons)}. ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C

NMR spectrum appeared complex): δ 160.20, 160.11, 159.41, 139.00, 138.72, 138.31, 138.12, 137.49, 136.61, 134.71, 133.76, 131.99, 131.81, 131.78, 131.62, 131.58, 131.19, 131.15, 131.13, 130.94, 130.85, 130.80, 130.76, 130.73, 129.98, 129.79, 129.67, 129.65, 129.63, 129.54, 129.43, 129.38, 129.18, 129.09, 128.76, 128.71, 128.65, 128.63, 128.54, 128.50, 128.24, 128.12, 128.02, 127.14, 126.84, 126.42, 126.15, 120.72, 119.95, 119.69, 119.03, 74.89, 74.41, 73.76, 73.55, 22.96, 22.67, 22.29, 22.08, 19.66, 19.56, 18.84, 18.72. HRMS (ESI) m/z calculated for $C_{39}H_{35}N_2$ $[M\text{-}BF_4]^+$ 531.2795, observed 531.2802.

Chloro[(1,2,3-n)-3-phenyl-2-propenyl][*4S*,*5S*-*1*,3-Bis(2,7-dimethylnaphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-imidazol-2-ylidene] palladium(II) [(DiPhSIMeNap)Pd(cin)Cl] (**2e**): DiPhSIMeNap·HBF_4 (320 mg, 0.52 mmol), KO^tBu (58 mg, 0.52 mmol) and $[Pd(cin)Cl]_2$ (134 mg, 0.26 mmol) were mixed together in a round flask in the glovebox. Dry THF (15 mL) was added and the mixture was stirred at room temperature for 14 h. The solvent was removed *in vacuo*, and the residue was separated by flash chromatography (SiO_2, 1:6→1:3 EtOAc/*n*-hexane) to afford two pure atropisomers (322 mg, 79%) (*One of the three atropisomers couldn't be isolated as a pure isomer*). Elemental analysis (%) calculated for $C_{48}H_{43}PdN_2Cl$: C, 73.01; H, 5.49; N, 3.55. Found: C, 73.21; H, 5.59; N, 3.55. HRMS (ESI) m/z calculated for $^{12}C_{48}H_{43}{}^{104}Pd^{14}N_2$ $[M\text{-}Cl]^+$ 753.2473, observed 753.2478.

Data for ***R*$_a$,*R*$_a$-2e** are as follows (first spot). (86 mg, 21%). Crystals suitable for diffraction studies were grown from a CH_2Cl_2/n-hexane solution of ***R*$_a$,*R*$_a$-2e**. $[\alpha]^{27}_D$ = -243.26 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (d, *J* = 17.1 Hz, 2H), 7.82-7.67 (m, 4H), 7.40-7.35 (m, 2H), 7.30-7.31 (m, 10H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.99-6.94 (br m, 3H), 6.82-6.81 (br m, 2H), 6.71-6.70 (br m, 2H), [5.97 (s) and 5.95 (s), 2H], 4.95-4.87 (m, 0.4H), 4.18-4.10 (m, 0.6H), 3.98 (d, *J* = 12.6 Hz, 0.4H), 3.92 (d, *J* = 12.6 Hz, 0.6H), 3.06 (d, *J* = 6.6 Hz, 0.4H), 2.85 (d, *J* = 6.6 Hz, 0.6H), 2.75 (s, 3H), 2.74 (s, 3H), 2.20 (s, 3H), 2.11 (s, 3H), 1.97 (d, *J* = 12.0 Hz, 0.6H), 1.05 (d, *J* = 12.0 Hz, 0.4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.44, 213.35, 138.66, 138.23, 136.64, 136.52, 136.25, 135.70, 135.53, 132.89, 131.72, 131.66, 131.33, 131.21, 129.35, 129.30, 129.22, 129.06, 128.70, 128.59, 128.45, 128.12, 128.04, 127.82, 127.75, 127.34, 127.22, 127.18, 126.45, 126.26, 123.52, 109.89, 109.56, 89.65, 87.60, 77.55, 77.23, 76.91, 74.64, 74.54, 48.62, 48.07, 22.52, 22.47, 19.64.

Data for R_a,S_a-**2e** are as follows (third spot). (236 mg, 58%). Crystals suitable for diffraction studies were grown from a EtOAc/n-hexane solution of R_a,S_a-**2e**. $[\alpha]^{27}_D$ = -265.16 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.88-6.72 (m, 23H), 6.44 (d, *J* = 8.2 Hz, 1H), 6.09-5.92 (m, 2H), 4.19-4.01 (m, 1H), 3.79-3.74 (m, 1H), [3.10 (s), 3.00 (s), 2.92 (s), 2.91 (s), 2.53 (s), 2.47 (s), 2.34 (s) and 2.16 (s), 12H], 2.97 (d, *J* = 8.2 Hz, 0.6H), 2.78 (d, *J* = 8.2 Hz, 0.4H), 1.48 (d, *J* = 12.0 Hz, 0.4H), 1.00 (d, *J* = 12.0 Hz, 0.4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.10, 213.26, 138.68, 138.49, 138.45, 136.35, 136.27, 136.22, 136.07, 135.91, 135.64, 135.33, 134.48, 134.22, 133.10, 132.96, 132.87, 132.11, 132.06, 131.57, 131.36, 131.23, 131.11, 129.51, 129.47, 129.39, 129.26, 129.23, 129.09, 128.84, 128.79, 128.74, 128.59, 128.52, 128.30, 128.23, 128.13, 127.85, 127,75, 127.41, 127.37, 127.16, 127.08, 126.97, 126.46, 126.37, 123.62, 123.36, 121.98, 121.76, 110.42, 109.60, 88.60, 87.22, 75.01, 74.76, 74.26, 49.86, 49.09, 31.80, 22.89, 22.26, 22.19, 21.39, 21.02, 20.69, 20.53, 14.32.

1*S*,2*S*-N,N′-Bis(2-isopropyl-6-adamantyl-naphthalen-1-yl)-1,2-diphenylethane-1,2-diamine. A 250 mL schlenk flask was charged with $Pd(dba)_2$ (288 mg, 0.50 mmol), (±)-BINAP (374 mg, 0.60 mmol), NaO^tBu (1.44 g, 15.00 mmol) and toluene (150 mL) and stirred for 20 min. 1-Bromo-2-isopropyl-6-adamantyl-naphthalene (4.22 g, 11.00 mmol) and (*1S,2S*)-(-)-1,2-diphenylethylenediamine (1.06 g, 5.00 mmol) were then added and the solution was heated to 110 °C for 20 h. After cooling to room temperature, the resulting mixture was filtered through a celite filter and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by flash chromatography (SiO_2, 1:4 CH_2Cl_2/*n*-hexane) to afford 1*S*,2*S*-N,N′-bis(2-isopropyl-6-adamantyl-naphthalen-1-yl)-1,2-diphenylethane-1,2-diamine as a white solid (1.50 g, 73%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.44 (d, *J* = 9.0 Hz, 2H), 7.65 (d, *J* = 2.0 Hz, 2H), 7.51-7.46 (m, 4H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.03-6.95 (m, 10H), 5.05 (br s, 2H), 4.76 (br s, 2H), 3.19 (sept, *J* = 6.8 Hz, 2H), 2.14 (br s, 6H), 2.02 (br s, 12H), 1.82 (br S, 12H), 1.16 (d, *J* = 6.8 Hz, 6H), 0.71 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.79, 140.75, 138.91, 137.82, 133.60, 128.78, 128.06, 128.02, 127.24, 124.18, 124.08, 124.02, 123.67, 123.49, 68.98, 43.34, 37.15, 36.34, 29.25, 27.90, 24.43, 22.88. HRMS (ESI) m/z calculated for $C_{60}H_{68}N_2Na$ $[M+Na]^+$ 839.5280, observed 839.5273.

***4S*,5*S*-*1*,3-Bis(2-isopropyl-6-adamantyl-naphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (DiPhSIPrAd*Nap·HBF$_4$) (1f).** Diamine 1*S*,2*S*-N,N′-bis(2-isopropyl-6-adamantyl-naphthalen-1-yl)-1,2-diphenylethane-1,2-diamine (900 mg, 1.10 mmol), ammonium tetrafluoroborate (139 mg, 1.32 mmol), triethyl orthoformate (1.80 mL, 11.00 mmol) and two drops formic acid were heated to 110 °C and stirred for 12 h. The resulting suspension was cooled down, and filtered to obtain a white solid. The excess ammonium tetrafluoroborate was removed by dissolving the solid in 10 ml CH_2Cl_2 and purging through a celite filter. The filtrate was concentrated and the product was obtained as a white solid (840 mg, 83%). $[\alpha]^{27}_D$ = -101.59 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) exists as a mixture of three atropisomers (15:31:54): δ {8.67 (s, NC*H*N), 8.54 (s, NC*H*N), 8.42 (s, NC*H*N) (correspond to the three atropisomers of a single proton)}, 8.26-7.25 (m, Ar*H*) (correspond to the three atropisomers of twenty two protons), {6.60 (s, NC*H*Ph), 6.59 (d, *J* = 12.8 Hz, NC*H*Ph), 6.26 (s, NC*H*Ph), 6.23 (d, *J* = 12.6 Hz, NC*H*Ph) (correspond to the three atropisomers of two protons)}, {3.80-2.97 (m, ArC*H*(CH_3)$_2$) (correspond to the three atropisomers of two protons)}, {2.24-0.68 (m, Ad and ArCH(C*H*$_3$)$_2$), (correspond to the three atropisomers of forty two protons)}. ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C NMR spectrum appeared complex): δ 159.05, 158.32, 158.27, 153.78, 150.46, 150.00, 145.81, 145.21, 143.54, 143.31, 133.35, 133.25, 132.87, 132.31, 132.24, 131.18, 131.10, 130.99, 130.25, 129.95, 129.68, 129.62, 129.59, 129.48, 129.32, 129.20, 129.14, 128.68, 128.36, 128.23, 127.85, 127.61, 126.85, 125.47, 124.89, 124.70, 124.46, 124.33, 123.81, 123.60, 123.54, 123.19, 121.95, 120.67, 120.00, 76.06, 75.68, 74.27, 73.64, 65.98, 43.16, 42.97, 42.95, 36.92, 36.90, 36.87, 36.74, 36.72, 36.45, 30.35, 29.83, 29.74, 29.07, 29.05, 28.97, 25.35, 24.71, 24.23, 22.48, 22.41, 22.02. HRMS (ESI) m/z calculated for $C_{61}H_{67}N_2$ $[M\text{-}BF_4]^+$ 827.5299, observed 827.5304.

Chloro[(1,2,3-n)-3-phenyl-2-propenyl][*4S*,*5S*-*1*,3-Bis(2-isopropyl-6-adamantyl-naphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-imidazol-2-ylidene] palladium(II) [(DiPhSIPrAd*Nap)Pd(cin)Cl] (**2f**): DiPhSIPrAd*Nap·HBF$_4$ (528 mg, 0.58 mmol), KO^{t}Bu (65 mg, 0.58 mmol) and [Pd(cin)Cl]$_2$ (142 mg, 0.28 mmol) were mixed together in a round flask in the glovebox. Dry THF (18 mL) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo*, and the residue was separated by flash chromatography (SiO_2, 1:9→1:3 EtOAc/*n*-

hexane) to afford two pure atropisomers (430 mg, 72%) (*One of the three atropisomers couldn't be isolated as a pure isomer*). Elemental analysis (%) calculated for $C_{48}H_{43}PdN_2Cl{\cdot}CH_2Cl_2$: C, 72.39; H, 6.60; N, 2.37. Found: C, 72.91; H, 6.37; N, 2.31. HRMS (ESI) m/z calculated for $^{12}C_{70}H_{75}{}^{104}Pd^{14}N_2$ $[M\text{-}Cl]^+$ 1049.4995, observed 1049.4982.

Data for ***R*$_a$,*R*$_a$-2f** are as follows (first spot). (167 mg, 28%). $[\alpha]^{27}_D$ = -272.39 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (br s, 2H), 7.85-7.72 (br m, 6H), 7.19-6.80 (m, 17H), 6.03 (br s, 2H), 5.04-5.03 (m, 0.6H), 4.40-4.08 (m, 1.4H), 3.59-3.48 (br m, 2.4H), 2.49-2.47 (br m, 0.6H), 2.17-1.22 (br m, 36.6H), 0.45-0.34 (br m, 6.4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.54, 148.45, 137.51, 136.59, 136.28, 133.28, 129.45, 129.22, 129.03, 128.39, 128.04, 127.18, 126.72, 124.65, 124.02, 109.07, 106.21, 91.81, 89.43, 88.59, 74.77, 53.63, 46.90, 43.34, 37.06, 36.46, 29.31, 29.16, 28.53, 25.82, 23.47.

Data for ***R*$_a$,*S*$_a$-2f** are as follows (third spot). (263 mg, 44%). $[\alpha]^{27}_D$ = -369.71 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.47-8.33 (m, 2H), 7.96-6.85 (m, 22H), 6.49 (br s, 1H), 6.24-6.13 (br m, 1H), 5.73 (d, *J* = 9.6 Hz, 1H), 4.46-3.44 (br m, 4H), [2.81 (br s) and 2.50 (br s), 1H], 2.26-0.63 (m, 40H), 0.43-0.27 (br m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.88, 148.45, 147.79, 146.73, 143.18, 138.77, 138.29, 137.67, 133.13, 132.33, 131.91, 129.95, 129.22, 129.08, 128.98, 128.78, 128.70, 128.58, 128.04, 127.93, 127.75, 127.41, 127.15, 126.19, 125.57, 125.32, 125.01, 124.92, 124.39, 123.55, 122.96, 122.54, 110.98, 108.99, 87.22, 53.62, 50.32, 49.98, 43.36, 43.27, 37.01, 36.98, 36.49, 36.26, 34.25, 30.08, 29.14, 29.07, 28.48, 26.32, 25.97, 25.72, 24.73, 24.57, 24.44, 24.26, 23.81, 22.46, 14.21.

1*S*,2*S*-N,N′-Bis(2,7-diisopropylnaphthalen-1-yl)-1,2-di-(3,5-dimethylphenyl)-ethane-1,2-diamine. A 250 mL schlenk flask was charged with $Pd(dba)_2$ (243 mg, 0.42 mmol), (±)-BINAP (318 mg, 0.51 mmol), NaO^tBu (1.22 g, 12.70 mmol) and toluene (150 mL) and stirred for 20 min. 1-Bromo-2,7-diisopropylnaphthalene (2.95 g, 10.20 mmol) and (*1S,2S*)-(-)-1,2-di-(3,5-dimethylphenyl)-ethylenediamine (1.14 g, 4.23 mmol) were then added and the solution was heated to 120 °C for 48 h. After cooling to room temperature, the resulting mixture was filtered through a celite filter and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by flash chromatography (SiO_2, 1:6 CH_2Cl_2/*n*-hexane) to afford 1*S*,2*S*-N,N′-bis(2,7-diisopropylnaphthalen-1-yl)-1,2-di-(3,5-dimethylphenyl)-ethane-1,2-diamine as a

white foam (1.90 g, 65%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.29 (s, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.69 (s, 2H), 6.64 (s, 4H), 4.90 (s, 2H), 4.83 (br s, 2H), 3.26 (sept, *J* = 6.9 Hz, 2H), 2.99 (sept, *J* = 6.9 Hz, 2H), 1.32 (d, *J* = 6.9 Hz, 6H), 1.29 (d, *J* = 6.9 Hz, 6H), 1.15 (d, *J* = 6.9 Hz, 6H), 0.67 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.97, 140.86, 139.24, 138.59, 137.18, 132.24, 129.76, 128.91, 128.51, 126.80, 124.85, 123.67, 123.49, 120.91, 68.75, 34.94, 28.02, 24.56, 24.55, 24.27, 22.88. HRMS (ESI) m/z calculated for $C_{50}H_{61}N_2$ $[M+H]^+$ 689.4829, observed 689.4839.

***4S*,*5S*-*1*,3-Bis(2,7-diisopropylnaphthalen-1-yl)-4,5-di-(3,5-dimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (Di(3,5-DiMePh)SIPrNap·HBF$_4$) (1g).** Diamine 1*S*,2*S*-N,N′-bis(2,7-diisopropylnaphthalen-1-yl)-1,2-di-(3,5-dimethylphenyl)-ethane-1,2-diamine (267 mg, 0.39 mmol), ammonium tetrafluoroborate (49 mg, 0.47 mmol), triethyl orthoformate (0.65 mL, 3.90 mmol) and two drops formic acid were heated to 120 °C and stirred for 16 h. The resulting mixture was dried *in vacuo*, and the residue was purified by flash chromatography (SiO_2, 1:20 MeOH:CH_2Cl_2) to afford the product as an off-white foam (255 mg, 84%). $[\alpha]^{27}_D$ = -84.26 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) exists as a mixture of three atropisomers (65:27:8): δ {8.88 (s, NC*H*N), 8.73 (s, NC*H*N), 8.72 (s, NC*H*N) (correspond to the three atropisomers of a single proton)}, 7.95-6.79 (m, Ar*H*) (correspond to the three atropisomers of sixteen protons), {6.32 (d, *J* = 12.0 Hz, NC*H*Ph), 6.26 (s, NC*H*Ph), 5.99 (s, NC*H*Ph), 5.92 (d, *J* = 12.0 Hz, NC*H*Ph) (correspond to the three atropisomers of two protons)}, 3.64-2.87 (m, ArC*H*$(CH_3)_2$), (correspond to the three atropisomers of four protons), 2.26-2.08 (m, PhCH_3), (correspond to the three atropisomers of twelve protons), {1.84-1.80 (m, ArCH(CH_3)$_2$), 1.62-1.15 (m, ArCH(CH_3)$_2$), 0.63-0.58 (m, ArCH(CH_3)$_2$), (correspond to the three atropisomers of twelve four protons)}. ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C NMR spectrum appeared complex): δ 159.76, 159.07, 158.48, 149.79, 149.66, 148.27, 146.41, 146.26, 144.03, 139.77, 139.41, 139.32, 132.86, 132.73, 132.67, 132.06, 131.96, 131.78, 131.26, 131.22, 130.80, 130.05, 129.78, 129.53, 128.47, 127.06, 126.99, 126.88, 126.70, 126.31, 125.99, 125.67, 124.68, 124.48, 123.35, 123.15, 119.06, 117.37, 116.36, 76.07, 73.60, 35.81, 35.36, 35.20, 30.43, 30.23, 30.08, 25.15, 25.09, 24.73, 24.67, 24.41, 24.21, 23.82,

22.52, 22.32, 21.93, 21.41, 21.30, 14.24. HRMS (ESI) m/z calculated for $C_{51}H_{59}N_2$ $[M\text{-}BF_4]^+$ 699.4673, observed 699.4683.

Chloro[(1,2,3-n)-3-phenyl-2-propenyl][*4S*,*5S*-*1*,3-Bis(2,7-diisopropylnaphthalen-1-yl)-4,5-di-(3,5-dimethyl-phenyl)-4,5-dihydro-imidazol-2-ylidene] palladium(II) [(Di(3,5-DiMePh)SIPrNap)Pd(cin)Cl] (**2g**): Di(3,5-DiMePh)SIPrNap·HBF_4 (560 mg, 0.70 mmol), KO^{t}Bu (80 mg, 0.71 mmol) and $[Pd(cin)Cl]_2$ (184 mg, 0.35 mmol) were mixed together in a round flask in the glovebox. Dry THF (30 mL) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo*, and the residue was separated by flash chromatography (SiO_2, 1:8→1:3 EtOAc/*n*-hexane) to afford three pure atropisomers (580 mg, 85%). Elemental analysis (%) calculated for $C_{60}H_{67}PdN_2Cl$: C, 75.22; H, 7.05; N, 2.92. Found: C, 75.59; H, 7.26; N, 2.92. HRMS (ESI) m/z calculated for $^{12}C_{60}H_{67}{}^{104}Pd^{14}N_2$ $[M\text{-}Cl]^+$ 921.4354, observed 921.4352.

Data for ***S*$_a$,*S*$_a$-2g** are as follows (first spot). (34 mg, 5%). $[\alpha]^{25}_D$ = 9.25 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (s, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.92-6.90 (br m, 7H), 6.71-6.67 (br m, 2H), 6.51-6.50 (br m, 2H), 5.72-5.68 (br m, 2H), 4.24-2.93 (br m, 7H), 2.08 (s, 12H), 1.77-1.19 (br m, 25H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.46, 145.45, 144.50, 143.87, 143.42, 138.91, 138.48, 137.69, 137.01, 136.64, 134.71, 132.95, 132.86, 132.37, 132.10, 131.47, 131.19, 130.53, 130.44, 129.30, 129.10, 128.03, 127.78, 127.67, 127.35, 127.16, 126.87, 126.70, 126.41, 126.13, 125.12, 124.64, 123.72, 123.34, 109.85, 109.40, 106.27, 91.90, 88.50, 87.07, 51.51, 49.57, 48.88, 35.01, 34.77, 34.49, 32.14, 29.92, 29.88, 29.58, 29.31, 28.91, 26.27, 26.10, 25.82, 24.76, 24.67, 24.45, 24.33, 24.15, 23.98, 23.76, 23.33, 22.91, 21.40, 14.33.

Data for ***R*$_a$,*R*$_a$-2g** are as follows (second spot). (403 mg, 59%). $[\alpha]^{23}_D$ = -306.54 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (br s, 2H), 7.81-6.60 (br m, 19H), 6.05 (br s, 2H), 5.17-5.09 (m, 0.6H), 4.45 (br s, 0.4H), 4.26-4.15 (m, 1H), 3.65 (br s, 2H), 3.41 (sept, *J* = 6.8 Hz, 2H), 2.67 (d, *J* = 5.4 Hz, 0.6H), 2.17 (br s, 12.4H), 1.70-0.88 (m, 19H), 0.58-0.49 (br m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.10, 146.66, 138.36, 137.85, 137.43, 131.84, 130.91, 130.72, 128.89, 128.45, 128.21, 128.09, 127.51, 127.19, 126.84, 126.66, 125.70, 125.00, 123.72, 108.84, 106.12, 92.52, 90.80, 89.12, 74.09, 64.57, 47.69, 46.42, 35.32, 34.82, 32.07, 31.73,

29.85, 29.81, 29.51, 29.21, 28.74, 28.52, 27.06, 26.15, 25.43, 25.20, 23.90, 23.15, 22.84, 22.80, 22.48, 21.34, 21.21, 20.86, 14.28, 11.59.

Data for ***R*$_a$,*S*$_a$-2g** are as follows (third spot). (143 mg, 21%). $[\alpha]^{23}_D$ = -315.15 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (s, 1H), 8.11 (br s, 1H), 7.91-6.59 (m, 19H), 5.95 (br s, 1H), 5.63 (br s, 1H), 4.51-2.60 (br m, 7H), 2.18-1.15 (br m, 34H), 0.40-0.24 (br m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.74, 212.62, 148.17, 147.26, 147.06, 145.15, 144.90, 144.45, 144.32, 138.67, 138.35, 138.10, 137.99, 137.45, 137.20, 136.57, 132.65, 132.29, 132.16, 132.04, 131.88, 131.81, 130.74, 130.60, 130.45, 129.54, 129.24, 128.83, 128.68, 128.57, 128.50, 128.34, 128.15, 128.00, 127.42, 127.25, 127.01, 126.34, 125.74, 124.89, 124.61, 124.36, 124.18, 123.85, 123.54, 123.26, 123.01, 122.79, 122.65, 121.21, 121.01, 109.77, 109.03, 106.10, 105,84, 89.29, 87.37, 81.99, 76.33, 76.12, 59.60, 52.94, 49.44, 48.40, 36.28, 36.05, 35.89, 34.88, 34.33, 32.14, 31.80, 29.97, 29.91, 29.87, 29.57, 29.27, 28.79, 28.69, 27.13, 26.43, 26.04, 25.49, 25.41, 25.32, 25.21, 24.97, 24.66, 24.41, 24.30, 24.18, 23.70, 22.90, 22.86, 22.54, 21.44, 21.33, 21.28, 20.92, 15.54, 14.33, 14.27, 11.64.

1*S*,2*S*-N,N′-Bis(2,7-diisopropylnaphthalen-1-yl)-1,2-di-(4-methoxylphenyl)-ethane-1,2-diamine. A 250 mL Schlenk flask was charged with $Pd(dba)_2$ (207 mg, 0.36 mmol), (±)-BINAP (274 mg, 0.44 mmol), NaO^tBu (1.06 g, 11.00 mmol) and toluene (120 mL) and stirred for 20 min. 1-Bromo-2,7-diisopropylnaphthalene (2.35 g, 8.10 mmol) and (*1S,2S*)-(-)-1,2-di-(4-methoxylphenyl)-ethylenediamine (1.00 g, 3.67 mmol) were then added and the solution was heated to 110 °C for 24 h. After cooling to room temperature, the resulting mixture was filtered through a celite filter and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by flash chromatography (SiO_2, 1:1 CH_2Cl_2/*n*-hexane) to afford 1*S*,2*S*-N,N′-bis(2,7-diisopropylnaphthalen-1-yl)-1,2-di-(4-methoxylphenyl)-ethane-1,2-diamine as a white foam (1.47 g, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (s, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 4H), 6.53 (d, *J* = 8.6 Hz, 4H), 4.91 (br s, 4H), 3.62 (s, 6H), 3.27 (sept, *J* = 6.9 Hz, 2H), 3.06 (sept, *J* = 6.9 Hz, 2H), 1.40 (d, *J* = 6.9 Hz, 6H), 1.33 (d, *J* = 6.9 Hz, 6H), 1.15 (d, *J* = 6.9 Hz, 6H), 0.64 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.71, 146.14, 139.50, 138.93, 133.10, 132.16, 130.08, 129.72, 128.55, 125.02, 124.15, 123.53, 120.75, 113.53, 68.47, 55.31, 34.93, 27.96, 24.70, 24.31,

22.86. HRMS (ESI) m/z calculated for $C_{48}H_{56}N_2O_2Na$ $[M+Na]^+$ 715.4239, observed 715.4230.

***4S*,*5S*-*1*,3-Bis(2,7-diisopropylnaphthalen-1-yl)-4,5-di-(4-methoxylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (Di(*p*-MeOPh)SIPrNap·HBF$_4$) (1h).** Diamine 1*S*,2*S*-N,N′-bis(2,7-diisopropylnaphthalen-1-yl)-1,2-di-(4-methoxylphenyl)-ethane-1,2-diamine (1.47 g, 2.11 mmol), ammonium tetrafluoroborate (266 mg, 2.54 mmol), triethyl orthoformate (3.51 mL, 21.10 mmol) and two drops formic acid were heated to 120 °C and stirred for 16 h. The resulting mixture was dried *in vacuo*, and the residue was purified by flash chromatography (SiO_2, 1:20 MeOH:CH_2Cl_2) to afford the product as an off-white foam (997 mg, 60%). $[\alpha]^{25}_D$ = -138.65 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) exists as a mixture of three atropisomers (53:10:37): δ {8.74 (s, NC*H*N), 8.53 (s, NC*H*N), 8.51 (s, NC*H*N) (correspond to the three atropisomers of a single proton)}, 7.94-6.69 (m, Ar*H*) (correspond to the three atropisomers of eighteen protons), {6.42 (d, *J* = 12.8 Hz, NC*H*Ph), 6.32 (s, NC*H*Ph), 6.11 (s, NC*H*Ph), 6.09 (d, *J* = 12.8 Hz, NC*H*Ph) (correspond to the three atropisomers of two protons)}, {3.73 (s, OCH_3), 3.71 (s, OCH_3), 3.63 (s, OCH_3), 3.61 (s, OCH_3) (correspond to the three atropisomers of six protons)}, 3.48-2.92 (m, ArC*H*$(CH_3)_2$), (correspond to the three atropisomers of four protons), 1.82-0.61 (m, ArCH$(CH_3)_2$), (correspond to the three atropisomers of twenty four protons). ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C NMR spectrum appeared complex): δ 161.83, 161.73, 161.57, 161.50, 159.06, 158.28, 150.06, 149.87, 148.54, 148.40, 146.57, 146.40, 144.70, 144.14, 132.04, 132.01, 131.86, 131.78, 131.52, 131.46, 130.63, 130.57, 130.43, 130.06, 130.02, 129.76, 129.56, 128.68, 128.49, 127.13, 126.74, 126.57, 125.84, 125.61, 125.42, 124.62, 124.39, 123.46, 123.34, 123.08, 122.44, 122.25, 122.07, 121.70, 118.97, 118.14, 117.08, 116.27, 115.47, 115.25, 115.07, 114.98, 75.33, 75.06, 73.49, 72.95, 66.02, 55.81, 55.77, 55.54, 35.60, 35.27, 35.20, 34.85, 34.31, 30.47, 30.12, 29.95, 25.34, 25.21, 24.88, 24.74, 24.66, 24.48, 24.43, 24.27, 24.22, 24.08, 23.93, 23.70, 22.52, 22.48, 22.15, 15.45, 14.24. HRMS (ESI) m/z calculated for $C_{49}H_{55}N_2O_2$ $[M-BF_4]^+$ 703.4258, observed 703.4263.

Chloro[(1,2,3-n)-3-phenyl-2-propenyl][*4S*,*5S*-*1*,3-Bis(2,7-diisopropylnaphthalen-1-yl)-4,5-di-(4-methoxyl-phenyl)-4,5-dihydro-imidazol-2-ylidene] palladium(II) [(Di(*p*-MeOPh)SIPrNap)Pd(cin)Cl] (**2h**): Di(*p*-MeOPh)SIPrNap·HBF$_4$ (408 mg,

0.52 mmol), KO^{t}Bu (58 mg, 0.52 mmol) and $[Pd(cin)Cl]_2$ (134 mg, 0.26 mmol) were mixed together in a round flask in the glovebox. Dry THF (10 mL) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo*, and the residue was separated by first flash chromatography (SiO_2, 1:12→1:3 EtOAc/*n*-hexane) to afford two pure atropisomers (376 mg, 76%) (*One of the three atropisomers couldn't be isolated as a pure isomer*). Elemental analysis (%) calculated for $C_{58}H_{63}PdN_2O_2Cl$: C, 72.41; H, 6.60; N, 2.91. Found: C, 72.20; H, 6.61; N, 2.84. HRMS (ESI) m/z calculated for $^{12}C_{58}H_{63}{}^{104}Pd^{14}N_2O_2$ $[M\text{-}Cl]^+$ 925.3938, observed 925.3937.

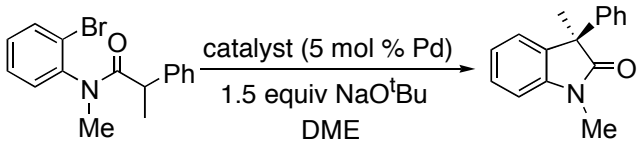
Data for ***R*$_a$,*R*$_a$-2h** are as follows (second spot). (223 mg, 45%). $[\alpha]^{24}_D$ = -334.29 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (br s, 2H), 7.81-6.55 (br m, 21H), 5.96 (br s, 2H), 5.12-5.04 (m, 0.6H), 4.42 (br s, 0.4H), 4.21-4.18 (m, 1H), 3.86 (s, 6H), 3.66-3.57 (br m, 2H), 3.31 (sept, *J* = 6.8 Hz, 2H), 2.64-2.63 (br m, 0.6H), 2.21-2.15 (br m, 0.4H), 1.73-1.24 (m, 19H), 0.51-0.45 (br m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.08, 160.27, 146.95, 137.44, 131.87, 130.84, 130.25, 129.03, 128.50, 128.28, 128.14, 127.54, 127.21, 126.73, 125.57, 114.28, 108.94, 104.39, 92.57, 73.81, 63.96, 55.51, 46.47, 35.27, 28.75, 26.16, 24.73, 23.99, 23.41, 18.12, 15.56.

Data for ***R*$_a$,*S*$_a$-2h** are as follows (third spot). (153 mg, 31%). $[\alpha]^{25}_D$ = -282.53 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (s, 1H), 8.00 (br s, 1H), 7.91-6.54 (m, 21H), 5.94 (br s, 1H), 5.76 (br s, 1H), 4.49-2.71 (br m, 13H), 1.84-1.19 (br m, 19H), 0.46-0.30 (br m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.15, 211.81, 211.48, 160.22, 159.79, 148.19, 148.08, 147.27, 147.08, 145.93, 145.17, 144.43, 138.37, 136.51, 132.34, 132.10, 131.91, 131.74, 131.15, 130.53, 130.27, 130.17, 129.84, 129.69, 129.56, 129.31, 129.21, 129.10, 128.85, 128.56, 128.41, 128.25, 128.12, 127.96, 127.71, 127.46, 127.39, 127.20, 126.31, 125.67, 124.85, 124.64, 124.29, 124.07, 123.86, 123.08, 122.77, 122.61, 121.12, 120.91, 113.87, 113.78, 109.92, 109.08, 105.87, 89.34, 89.04, 87.43, 76.46, 76.27, 76.05, 75.52, 75.35, 55.51, 55.26, 52.78, 49.34, 48.55, 39.32, 36.14, 35.86, 34.46, 34.13, 32.10, 29.91, 29.54, 28.64, 28.51, 26.52, 26.02, 25.55, 25.39, 25.19, 24.68, 24.55, 24.04, 23.93, 23.74, 23.48, 22.87, 14.30.

Bimetallic palladium complex [{$PdCl_2$((*R*$_a$,*R*$_a$)-(*4S*,*5S*)-DiPhSIPrNap)}$_2$] (6): In a 20 mL vial, complex ***R*$_a$,*R*$_a$-2a** (100 mg, 0.12 mmol) was added and put under

nitrogen atmosphere. To this, 10 mL Et_2O and 4.0M HCl in dioxane (1 mL) were added. The resultant suspension was stirred for 1h, filtered through a cotton filter, and washed by Et_2O (5 mL). The solid was collected by washing with 5 mL CH_2Cl_2, and dried *in vacuo* to give the dimeric complex **5** (87 mg, 96%). Crystals suitable for diffraction studies were grown from a $CHCl_3$/pentane solution of **5**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (s, 2H), 7.81-7.71 (m, 8H), 7.60 (s, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.19-7.06 (m, 16H), 7.00 (t, *J* = 7.7 Hz, 4H), 6.86 (d, *J* = 7.5 Hz, 4H), 3.52 (sept, *J* = 6.6 Hz, 2H), 3.20 (sept, *J* = 6.7 Hz, 4H), 3.01 (sept, *J* = 6.9 Hz, 2H), 1.45 (d, *J* = 6.9 Hz, 6H), 1.44 (d, *J* = 6.7 Hz, 6H), 1.40 (d, *J* = 6.6 Hz, 6H), 1.33 (d, *J* = 6.9 Hz, 6H), 1.27 (d, *J* = 6.9 Hz, 6H), 0.99 (d, *J* = 6.7 Hz, 6H), 0.28 (d, *J* = 6.6 Hz, 6H), 0.24 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.88, 147.46, 147.11, 146.66, 145.97, 136.57, 135.54, 131.91, 130.38, 130.16, 130.09, 129.92, 129.66, 129.45, 129.31, 129.29, 129.08, 129.00, 128.84, 128.80, 128.66, 128.39, 125.10, 125.06, 124.03, 123.90, 123.72, 121.98, 73.60, 72.77, 35.28, 35.14, 28.65, 28.54, 27.06, 26.68, 24.69, 24.65, 23.99, 23.80, 23.76, 23.31.

Catalytic results for asymmetric intramolecular α-arylation of 3a catalyzed by 2a versus (SIPr)Pd(cin)Cl:



3a **4a**

entry	catalyst	temperature	time	% yield[a] (% ee[b,c])
1	(R_a,R_a)-**2a**	23°C	12h	98 (86)
2	(R_a,S_a)-**2a**	23°C	4h	98 (67)
3	(S_a,S_a)-**2a**	23°C	6h	98 (20)
4	(SIPr)Pd(cin)Cl	23°C	32h	73[d](--)

[a]Isolated yields. [b]Determined by chiral HPLC. [c]Absolute stereochemistry determined as (*R*)-configuration, see ref. 9d. [d] GC yield.

Pd catalyzed asymmetric intramolecular α-arylation to give oxindoles 3a-g:

Gerneral procedure: Catalyst (5 mol%) and base (1.5 eq.) were charged in a 20 mL vial in a glovebox. DME (2 mL) was added and the mixture was stirred for 5 min. The 2-bromo-N-alkylanilide (0.2 mmol, 1 eq.) was then added as a solution in 2 mL DME. The reaction was stirred at room temperature or 50 °C, and monitored by GC-MS. After the required time, the reaction was treated with aq. NH_4Cl and this phase was extracted with 2×15 mL ether. The combined organic phases were washed with brine

and dried over $MgSO_4$. Flash chromatography afforded the product oxindoles. The enantiomeric purity of products **4a-g** was determined by chiral HPLC analysis.

(*R*)-**4a**:[9] colorless oil, 98% yield. 86% ee [Chiracel OD-H column, *n*-hexane/*i*-PrOH = 99:1, 1.0 mL/min, t_R = 15.04 min (minor) and 18.08 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.18 (m, 5H), 7.16-7.14 (m, 1H), 7.11-7.09 (m, 1H), 7.00 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.15 (s, 3H), 1.70 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.61, 143.42, 140.98, 135.00, 128.69, 128.28, 127.38, 126.81, 124.37, 122.94, 108.46, 52.31, 26.63, 23.93. HRMS (EI) m/z calculated for $C_{16}H_{15}NO$ $[M]^+$ 237.1154, observed 237.1151.

(*R*)-**4b**:[9] colorless oil, 98% yield. 88% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 97:3, 1.0 mL/min, t_R = 10.17 min (minor) and 11.43 min (major)] (racemic sample was prepared by using SIPrNapPd(allyl)Cl as catalyst); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.22 (m, 10H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.05 (dt, *J* = 7.7, 1.0 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.94 (dd, *J* = 28.8, 15.6 Hz, 2H), 1.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.69, 142.46, 141.00, 136.17, 135.15, 128.94, 128.76, 128.15, 127.75, 127.43, 127.39, 126.83, 124.36, 122.98, 109.53, 52.32, 43.99, 23.98. HRMS (EI) m/z calculated for $C_{22}H_{19}NO$ $[M]^+$ 313.1467, observed 313.1469.

(*R*)-**4c**:[9] colorless oil, 99% yield. 87% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 97:3, 1.0 mL/min, t_R = 8.85 min (minor) and 9.96 min (major)] (racemic sample was prepared by using SIPrNapPd(allyl)Cl as catalyst); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.20-7.17 (m, 3H), 7.11-7.06 (m, 3H), 6.90 (d, *J* = 7.7 Hz, 1H), 3.22 (s, 3H), 2.29 (s, 3H), 1.77 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.76, 143.45, 138.03, 137.06, 135.17, 129.40, 128.20, 126.69, 124.32, 122.90, 108.41, 52.01, 26.62, 23.93, 21.12. HRMS (EI) m/z calculated for $C_{17}H_{17}NO$ $[M]^+$ 251.1310, observed 251.1313.

(*R*)-**4d**:[9] colorless oil, 97% yield. 89% ee [Chiracel OD-H column, *n*-hexane/*i*-PrOH = 98:2, 1.0 mL/min, t_R = 15.96 min (minor) and 22.95 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (t, *J* = 7.9 Hz, 1H), 7.30-7.25 (m, 2H), 7.18 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 3.31 (s, 3H), 1.77 (s, 3H), 1.61 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.15, 143.14, 138.05, 136.98, 135.24, 131.85, 127.96, 127.83, 127.57, 126.16, 123.11, 123.04, 108.21, 52.48, 26.60, 25.94, 19.35. HRMS (EI) m/z calculated for $C_{17}H_{17}NO$ $[M]^+$ 251.1310, observed 251.1306.

(*R*)-**4e**:[9] colorless oil, 99% yield. 80% ee [Chiracel OD-H column, *n*-hexane/*i*-PrOH = 98:2, 1.0 mL/min, t_R = 11.04 min (minor) and 12.73 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.12-7.04 (m, 4H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.24 (s, 3H), 2.30 (s, 3H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.72, 143.38, 140.87, 138.28, 135.19, 128.54, 128.19, 127.45, 124.31, 123.82, 122.91, 108.42, 52.25, 26.62, 23.88, 21.73. HRMS (EI) m/z calculated for $C_{17}H_{17}NO$ $[M]^+$ 251.1310, observed 251.1311.

(*R*)-**4f**:[9] white solid, 93% yield. 85% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 97:3, 1.0 mL/min, t_R = 22.97 min (minor) and 53.27 min (major)] (racemic sample was prepared by using SIPrNapPd(allyl)Cl as catalyst); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.54 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.34-7.28 (m, 2H), 7.17-7.13 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.92 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 7.0 Hz, 1H), 3.43 (s, 3H), 1.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.64, 142.40, 136.95, 135.31, 134.58, 131.55, 129.32, 129.25, 128.10, 126.45, 125.44, 125.27, 123.69, 123.28, 123.05, 108.79, 52.66, 27.01, 26.89. HRMS (EI) m/z calculated for $C_{20}H_{17}NO$ $[M]^+$ 287.1310, observed 287.1307.

(*R*)-**4g**:[9] white solid, 93% yield. 84% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 97:3, 1.0 mL/min, t_R = 20.46 min (minor) and 40.32 min (major)] (racemic sample was prepared by using SIPrNapPd(allyl)Cl as catalyst); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.58-7.51 (m, 3H), 7.42-7.30 (m, 4H), 7.20 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 6.8 Hz, 1H), 6.90-6.81 (m, 3H), 5.11 (dd, *J* = 94.8, 15.2 Hz, 2H), 1.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.48, 141.46, 136.96, 136.26, 135.29, 134.54, 131.51, 129.33, 129.17, 129.02, 128.49, 128.06, 127.93, 126.49, 126.33, 125.48, 125.26, 124.23, 123.24, 123.09, 109.76, 52.64, 44.50, 27.26. HRMS (EI) m/z calculated for $C_{26}H_{21}NO$ $[M]^+$ 363.1623, observed 363.1622.

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(7) Different rotamers of NHC salts and precatalysts seem to exist, see supporting information of refs. 4a and 5b.

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(12) R_a/S_a denote the axial chirality between the N-heterocycle and the naphthyl side chains.

(13) **2a** performs better than the reference system (SIPr)Pd(cin)Cl, see the experimental part.

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Chapter 4

Highly Chemo- and Enantioselective Synthesis of 3-Allyl-3-Aryl Oxindoles via the Direct Palladium-Catalyzed α-Arylation of Amides

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4.1 Abstract

A new NHC•Pd-catalyzed asymmetric a-arylation of amides is reported giving direct access to synthetically valuable, allylated oxindoles with quaternary carbon centers. The reaction is made possible by the introduction of a new chiral NHC ligand. The palladium complexes derived thereof combine excellent reactivity with high chemo- and enantioselectivity for the title transformation.

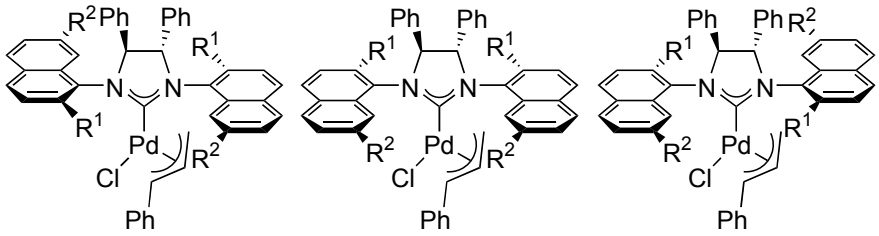
4.2 Introduction

Oxindoles bearing a quaternary carbon stereocenter at the 3-position represent a prominent structural motif in a range of alkaloid natural products,[1] and pharmaceutical compounds,[2] and the development of synthetic methods for these compounds, including the ones with new substitution patterns, is therefore of high importance in organic chemistry. Consequently, several transition-metal-catalyzed enantioselective approaches were established over the last decade: Overman's elegant intramolecular Heck reactions,[1b-c,3] Trost's Pd- or Mo-mediated allylic alkylations,[4] Pd-catalyzed intra- and intermolecular arylations pioneered by Hartwig,[5] and Buchwald,[6] Takemoto's Pd-catalyzed cyanoamidation protocol,[7] and most recently, Stoltz's Cu-catalyzed alkylations.[8]

As part of our ongoing research on employing chiral monodentate *N*-heterocyclic carbene (NHC) ligands for metal-catalyzed asymmetric catalysis, we recently reported the synthesis of diastereomerically pure palladium complexes incorporating new chiral NHC ligands and their successful application in the Pd-catalyzed intramolecular α-arylation of amides to obtain enantiomerically enriched 3-aryl-3-methyl oxindoles.[5c] While elegant as a methodology to obtain chiral quaternary carbon centers, the intramolecular α-arylation at present has the drawback of providing oxindoles that are difficult to functionalize further. We therefore wondered whether 3-allyl-3-aryl oxindoles, previously only accessible via a two-step procedure involving a Pd-catalyzed intramolecular α-arylation followed by an asymmetric Pd-catalyzed allylic alkylation,[4a,9] could be obtained directly. Herein we report the successful achievement of this strategy by using a newly designed NHC ligand.

4.3 Results and Discussion

Our investigation commenced by examining the ability of NHC•Pd complexes **1a-c** (Scheme 1), previously developed in our laboratories,[5c] to promote the intramolecular α-arylation of the model substrate **2a**. At the outset of the study and under the reaction conditions used, it was not clear whether such α-arylations would be preferred over a reaction scenario involving Heck cyclizations giving rise to 7-exo-trig (or 8-endo-trig) products. The catalytic results reported in Table 1 indeed indicate that Heck cyclization is competitive and product **4a** was formed in noticeable amounts (15-20%) with all diastereomers of precatalysts **1a-c**. Trends in enantioselectivity though were immediately apparent. Somewhat surprising was the fact that the diastereomers of catalyst **1a**, which performed best in our previous investigation, gave erratic results with inconsistent absolute configurations of product **3a**. In fact, omitting the R^2-isopropyl group on the naphthyl wingtips of the NHC (precatalysts **2b**) gave more usable results (Entries 4/5). Furthermore, precatalyst **1c** that incorporates a slightly bulkier R^2-cyclohexyl group resulted in better enantioselection (Entries 6/7). Although both the chemoselectivity as well as the enantioselectivity (66% ee) were still not practical, the simple fact that representative chiral mono- and bidentate phosphorus ligands showed inferior results (see the Supporting Information) suggested that complexes **1a-c** contained the more promising overall catalyst motif.



R_a,R_a-**1a** R_a,S_a-**1a** S_a,S_a-**1a**

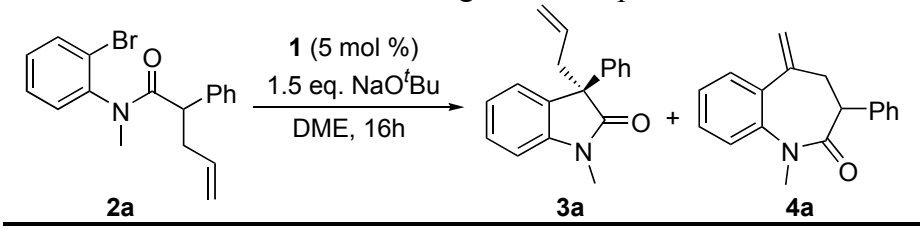
R_a,R_a-**1b** R_a,S_a-**1b**

R_a,R_a-**1c** R_a,S_a-**1c**

1a: $R^1 = R^2 = {}^i$Pr **1b**: $R^1 = {}^i$Pr, R^2 = H **1c**: R^1 = Cy, R^2 = H

Scheme 1. Previously reported palladium complexes **1a-c**.

Table 1. Initial screening of Pd-complexes **1a-c**.

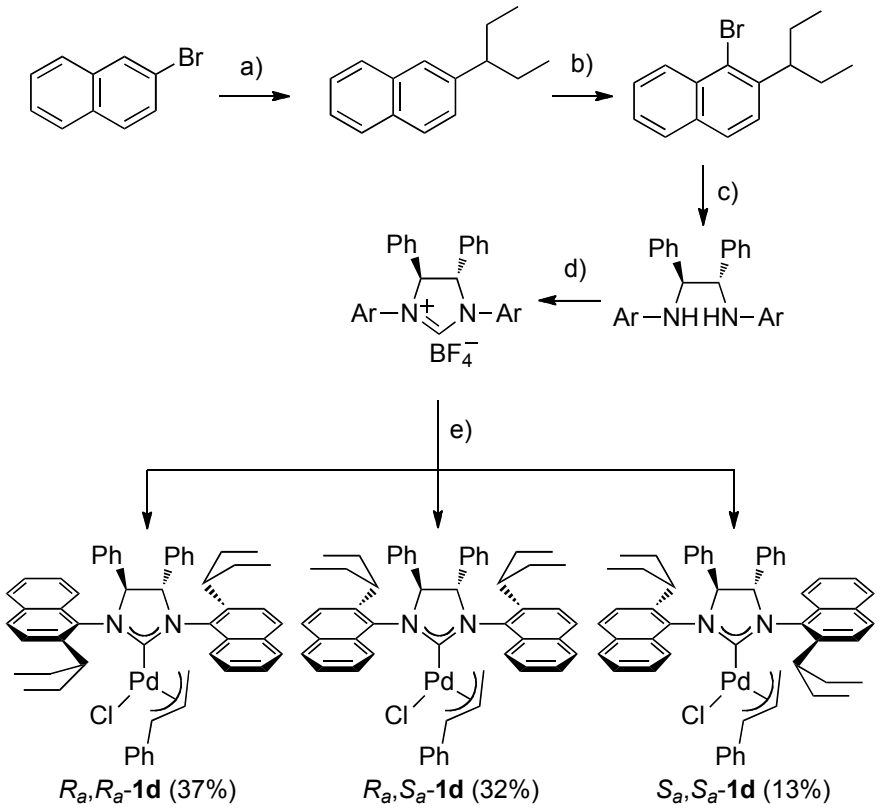


2a **3a** **4a**

Entry	NHC•Pd	*T* (°C)	Conv [%][a]	**3a**/**4a**[b]	ee [%][c,d]
1	R_a,R_a-**1a**	23	>99	5:1	-24 (*S*)
2	R_a,S_a-**1a**	23	>99	4:1	56 (*R*)
3	S_a,S_a-**1a**	23	>99	5:1	34 (*R*)
4	R_a,R_a-**1b**	50	>99	4:1	39 (*R*)
5	R_a,S_a-**1b**	50	>99	4:1	58 (*R*)
6	R_a,R_a-**1c**	50	>99	6:1	46 (*R*)
7	R_a,S_a-**1c**	50	>99	4:1	**66 (*R*)**

[a] Determined by GC-MS. [b] Determined by analysis of ^{1}H NMR spectra of product mixtures prior to purification. [c] Determined by chiral HPLC for **3a**. [d] The absolute configuration of **3a** was assigned according to ref 10.

The tendencies in selectivity observed in Table 1 were subsequently implemented in the design of a modified chiral NHC structure that lacks the R^2 wingtip group and incorporates a bulkier, unstrained 3-pentyl moiety on the 2-position of the naphthyl side chains. We were hoping that the bulkier group would help transfer the chiral information more effectively from the NHC backbone to the side chains, and hence induce higher enantioselectivity. The precursor imidazolinium salt was obtained relatively easily via the four-step synthetic procedure outlined in Scheme 2. Subsequent deprotonation, reaction with $[Pd(cin)Cl]_2$ and column chromatographic workup gave precatalyst **1d** in 82% yield as three separable diastereomers [R_a,R_a-**1d** (37%), R_a,S_a-**1d** (32%) and S_a,S_a-**1d** (13%)].

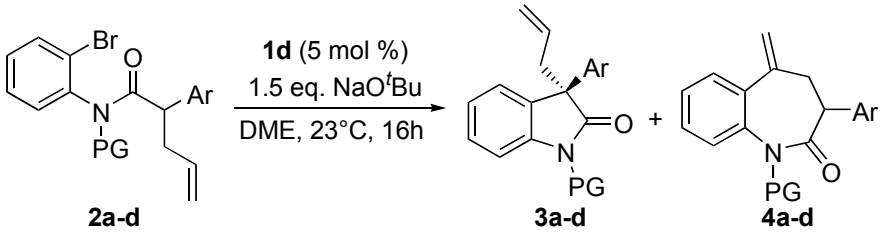


Scheme 2. Synthesis of complexes **1d** bearing a newly designed NHC ligand. Reaction conditions: a) Mg/THF, 3-bromopentane, $(FeCl_3)_2(TMEDA)_3$ (2.5 mol%), THF, 70%.[11] b) Br_2 (1 eq.), CH_2Cl_2, -78°C, 24h, 97%. c) $Pd(dba)_2$ (5 mol%), (±)-BINAP (6 mol%), NaO^{t}Bu, (*1S,2S*)-(-)-1,2-diphenylethylenediamine, Toluene, 120°C, 48h, 57%. d) $HC(OEt)_3$, NH_4BF_4, 120°C, 16 h, 84%. e) $[Pd(cin)Cl]_2$ (0.5 eq.), KO^{t}Bu, THF, rt, 16h, 82%.

In a first test, these new catalysts were subjected to our standard substrate **2a** (Table 2, Entries 1-3). The results were very encouraging and all three diastereomeric precatalysts **1d** proved superior to their congeners **1a-c** both in terms of their higher reactivity (room temperature) and their enhanced selectivity. As an unexpected and very welcome side effect, incorporation of the new NHC ligand also greatly enhanced the chemoselectivity of the transformation with generation of only trace amounts (if any) of Heck byproduct **4a**. As a consequence, treatment of **2a** in the presence of 5 mol % R_a,R_a-**1d** gave rise to oxindole **3a** in 96% isolated yield and 81% ee. Because both catalysts R_a,R_a-**1d** and R_a,S_a-**1d** showed identical enantiomeric excesses with substrate **2a** and before embarking in a thorough substrate scope study, we examined the two catalysts with three other substrates, varying both the aromatic group at the α-

carbon as well as the protecting group at nitrogen (Table 2, Entries 4-11). The results indicated that R_a,R_a-**1d** was overall giving better chemoselectivities and evenly high enantiomeric excesses with all four substrates, thereby outperforming R_a,S_a-**1d** (Exception; Entries 7/8, see discussion below).

Table 2. Identification of the optimal catalyst.



2a-d **3a-d** **4a-d**

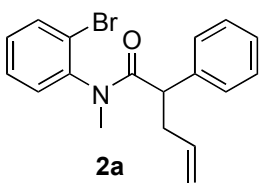
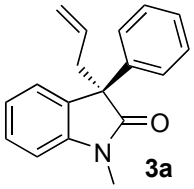
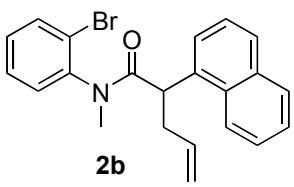
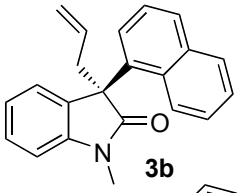
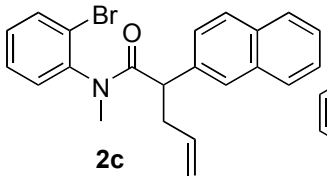
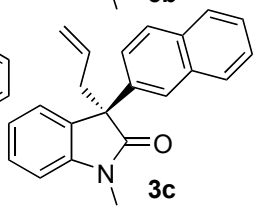
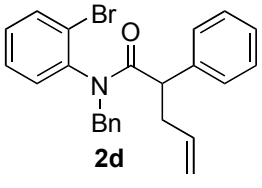
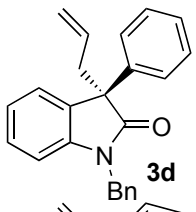
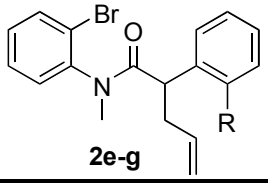
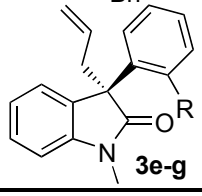
Entry	NHC•Pd	Substrate (Ar, PG)	**3**/**4**[a]	Yield [%][b]	ee [%][c]
1	R_a,R_a-**1d**	**2a** (Ph, Me)	10:0	96	**81 (*R*)**
2	R_a,S_a-**1d**	**2a** (Ph, Me)	16:1	90	81 (*R*)
3	S_a,S_a-**1d**	**2a** (Ph, Me)	10:0	93	52 (*R*)
4	R_a,R_a-**1d**	**2b** (1-Napht, Me)	10:0	98	**87 (*R*)**
5	R_a,S_a-**1d**	**2b** (1-Napht, Me)	17:1	88	39 (*R*)
6	S_a,S_a-**1d**	**2b** (1-Napht, Me)	19:1	91	53 (*R*)
7	R_a,R_a-**1d**	**2c** (2-Napht, Me)	10:0	98	**82 (*R*)**
8	R_a,S_a-**1d**	**2c** (2-Napht, Me)	18:1	90	85 (*R*)
9	S_a,S_a-**1d**	**2c** (2-Napht, Me)	10:0	97	56 (*R*)
10	R_a,R_a-**1d**	**2d** (Ph, Bn)	10:1	86	**81 (*R*)**
11	R_a,S_a-**1d**	**2d** (Ph, Bn)	8:1	83	63 (*R*)

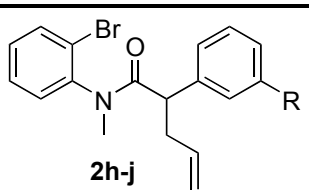
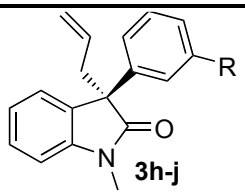
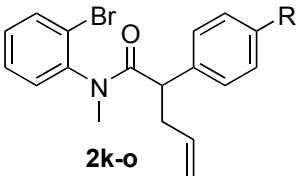
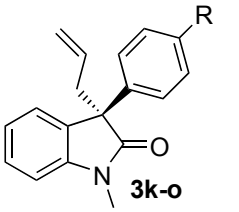
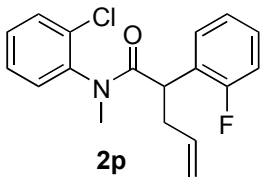
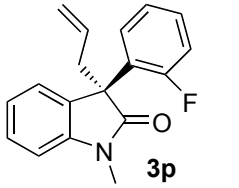
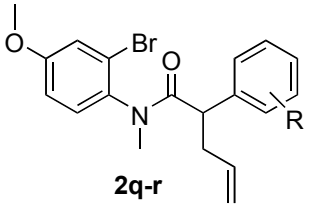
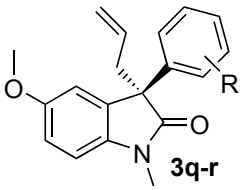
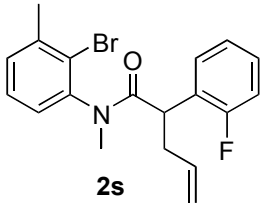
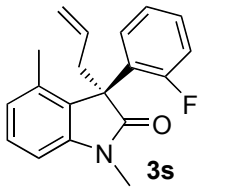
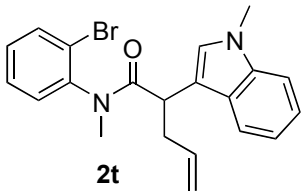
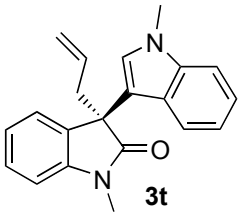
[a] Determined by analysis of ^{1}H NMR spectra of product mixtures prior to purification. [b] Isolated yields of **3a-d**. [c] Determined by chiral HPLC for **3a-d**.

With the optimized catalyst in hand, we sought to examine the scope of the reaction. Thus, an important number of different amides were synthesized and subjected to the standard reaction conditions (5 mol % R_a,R_a-**1d**, 1.5 eq. NaO^{t}Bu, DME, 23°C, 16h). Results in Table 3 show that broad structural variations in the amide system can be accommodated. In nearly all cases, excellent yields, virtually complete chemoselectivities and good-to-excellent enantioselectivities were obtained. For example, *ortho*-substituted aromatic groups are tolerated, and the sterically demanding products were obtained with selectivities of up to 91 % ee (Entry 5). The method is compatible with both electron-rich and electron-poor aromatic groups, and *ortho*-, *meta-,* as well as *para*-positions could be varied (Table 4, Entry 4-15). We also examined two substrates containing a 5-methoxy group, a motif commonly found in bioactive oxindole-based compounds, with equally satisfying results (Entries 17,18). Furthermore, the remarkable reactivity of catalyst R_a,R_a-**1d** allows the reaction

with less reactive aryl chlorides to proceed at room temperature with high yield and ee (Entry 16).[5a,d,e] Limitations became only apparent when the sterically highly congested substrate **2s** was tested. Here, a complete loss of enantioselectivity was accompanied with lower than normal reactivity (Entry 19). Nevertheless, the simple fact that catalyst R_a,S_a-**1d** could promote such a difficult C–C coupling at room temperature is noteworthy. Substrate **2t** containing a heteroaromatic *N*-Me-3-indolyl moiety also undergoes smooth cyclization to give oxindole **3t** (94% yield, 86% ee, Entry 21). Contrary to what has been described,[12] the possible indolo-benzazepine byproduct arising from competitive Heck cyclization of the indolyl group was not observed. The framework of **3t** is of particular synthetic interest as it is widely found in natural products, and a range of total syntheses have been carried out based on this type of core structure.[2a-b]

Table 3. Scope of asymmetric synthesis of oxindoles with R_a,R_a-**1d**.

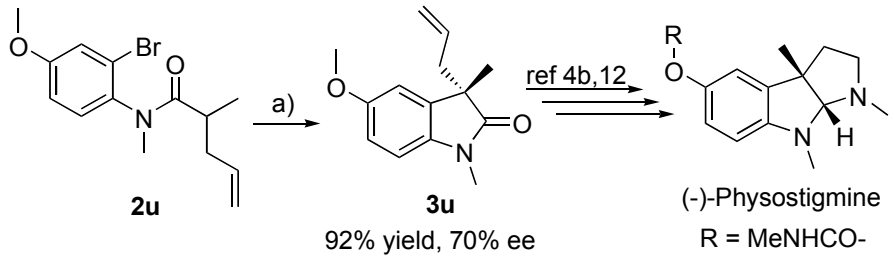
Entry	Substrate	Product	R	Yield [%][a]	ee [%][b]
1	 **2a**	 **3a**		96	81
2	 **2b**	 **3b**		98	87
3	 **2c**	 **3c**		98	82
4	 **2d**	 **3d**		86	81
5	 **2e-g**	 **3e-g**	Me	97	85
6			F	94	91
7			MeO	92	83

8	 **2h-j**	 **3h-j**	Me	93	77
9			F	98	79
10			MeO	91	80
11	 **2k-o**	 **3k-o**	Me	94	82
12			F	94	83
13			MeO	89	77
14			CF_3	97	86
15			Ph	95	87
16	 **2p**	 **3p**		90	86
17	 **2q-r**	 **3q-r**	*o*-F	91	94
18			*p*-Ph	90	88
19	 **2s**	 **3s**		40	8
20[c]				95	2
21	 **2t**	 **3t**		94	86

[a] Isolated yields of **3**. [b] Determined by chiral HPLC for **3**, and the absolute configuration of **3** is depicted. [c] Catalyst R_a,S_a-**1d** was used to replace catalyst R_a,R_a-**1d**.

To exemplify the generality of the present protocol and highlight catalyst **1d**'s excellent performance, substrate **2u** with two alkyl substituents at the α-position of the carbonyl moiety was also tested. The reaction with this more challenging substrate once again proceeded smoothly at ambient temperature to give oxindole **3u** with acceptable levels of enantioselectivity and excellent chemoselectivity (>20:1). To our knowledge, this is the first successful example of preparing enantiomerically enriched 3,3'-dialkyl oxindoles via a Pd-catalyzed α-arylation protocol,[13] and Scheme 3

underlines the importance of **3u** as a key intermediate for the synthesis (-)-physostigmine.[4b,14]



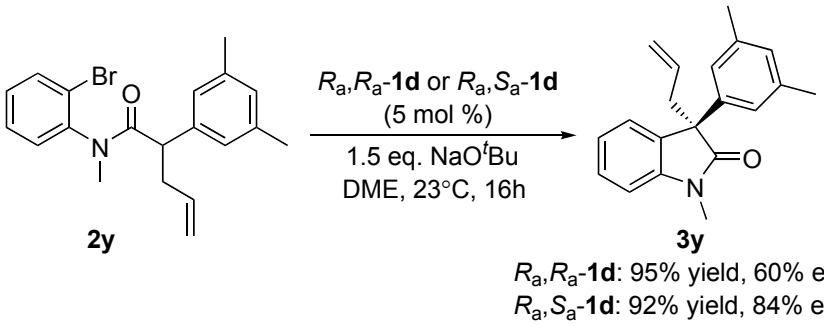
Scheme 3. Enantioselective synthesis of 3,3'-dialkyl oxindole **3x** and its related natural product. Condition: (a) 5 mol % R_a,R_a-**1d**, 1.5 eq. NaO^{t}Bu, DME, 23°C, 16h.

A last question that we wanted to answer stemmed from our preliminary runs in Table 2. Data showed that catalyst R_a,S_a-**1d** performed slightly better for substrate **2c** than R_a,R_a-**1d** and we were therefore wondering whether the same trend is followed with substrates **2h-j** that also contain *meta*-substituted aromatic moieties. Results in Table 4 indeed point to a general trend for these substrates with slightly higher enantiomeric excesses when employing R_a,S_a-**1d**. Differences in selectivity are further amplified with sterically more demanding, doubly *meta*-substituted amide **2y** (Scheme 4). Together with simple molecular models of both catalysts R_a,S_a-**1d** and R_a,R_a-**1d**, these last results provided valuable indications on the enantioselection process that might be at play in the present catalytic system.

Table 4. R_a,S_a-**1d** versus R_a,R_a-**1d** with *meta*-substituted substrates.

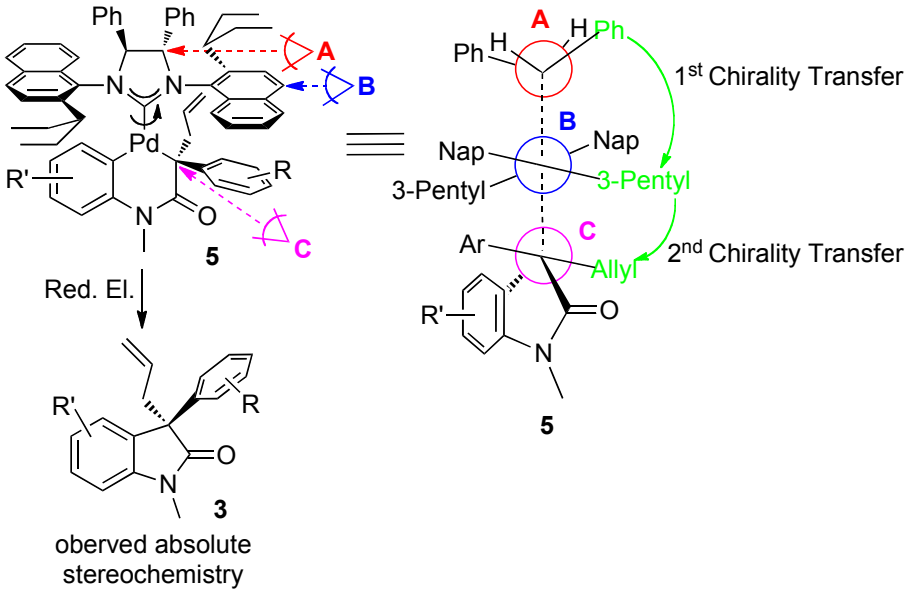
Entry	Substrate	Product	Yield [%][a]	ee [%][b,c]
1	**2c**	**3c**	94	85 vs (82)
2	**2h**	**3h**	91	83 vs (77)
3	**2i**	**3i**	97	85 vs (79)
4	**2j**	**3j**	90	85 vs (80)

[a] Isolated yields. [b] Determined by chiral HPLC. [c] The values in brackets were obtained with catalyst R_a,R_a-**1d**.



Scheme 4. R_a,R_a-**1d** and R_a,S_a-**1d** catalyzed formation of oxindole **3v**.

In analogy to the postulated model for the asymmetric synthesis of 3-aryl-3-methyl oxindoles involving members of catalyst family **1**,[5c] the key event for enantiodiscrimination involves the carbon-palladium bond formation that leads to intermediate **5** (Scheme 5) and the relative orientation of the groups on the deprotonated α-carbon of the amide during this step. Simple molecular modeling of **5** showed that the allyl moiety neatly resides on the same side of the 3-pentyl unit of the NHC framework, while the aromatic moiety is accommodated on the opposite, more open side of the naphthyl moiety. Discrimination in these ligands is therefore initiated via chirality transfer from the chiral backbone of the NHC ligand (**A**) to the 2-position (3-pentyl group) of the naphthyl side chains (**B**) which subsequently distinguish the different substrate groups during the bond formation step that leads to intermediate **5** (**C**). The erosion in enantioselectivity with catalyst R_a,R_a-**1d** and *meta*-substituted aryl substrates such as **2v** seems to originate from a strong repulsion between the *meta*-position of the aromatic unit and the 3-pentyl group on the opposite side chain of the R_a,R_a-configured NHC ligand. Indeed, the repulsion is absent when switching to catalyst R_a,S_a-**1d**, therefore providing compound **3v** with higher enantioselectivity (84% ee).



Scheme 5. Proposed model for enantiodiscrimination.

4.4 Conclusion

In conclusion, we have devised a new synthetic strategy to access functionalizable 3-allyl oxindoles bearing a chiral quaternary carbon stereocenter via

a direct palladium-catalyzed α-arylation protocol. Impressive reactivities and high chemo- and enantioselectivities were achieved through the use of a new chiral N-heterocyclic carbene ligand structure. Diastereomerically pure palladium complex R_a,R_a-**1d** proved to be the most general catalyst for the transformation and gave enantiomerically enriched oxindoles with selectivities of up to 94% ee. For making oxindoles bearing *meta*-substituted aromatic groups at the 3-position, catalyst R_a,S_a-**1d** was found to be slightly more efficient. A mechanistic model is proposed that rationalizes the catalytic results and explains the enantioselection pathway.

Acknowledgment. R.D. holds an Alfred Werner Assistant Professorship and thanks the foundation for generous financial support. X.L. thanks UZH (through a Drittmittelkredit) for support.

Supporting Information Available: Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

4.5 Experimental Part

General Information. All reactions were carried out under a nitrogen atmosphere using Standard Schlenk-Lines or gloveboxes (Mecaplex or Innovative Technology). All reagents were used as received unless otherwise noted. Solvents were purchased in the best quality available, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Solvents for NMR spectroscopy were degassed with nitrogen and dried over molecular sieves. NMR spectra were recorded on AV2 400 or AV2 500 MHz Bruker spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^{1}H and ^{13}C signals of the solvents. Coupling constants J are quoted in Hz. Analytical HPLC analyses were performed using a JASCO series PU-2089/MD-2010 apparatus with a chiral stationary phase (see details where applies). High-resolution electrospray ionization mass spectrometry was performed on a *Finnigan MAT 900* (*Thermo Finnigan*, San Jose, CA; USA) double-focusing magnetic sector mass spectrometer. 10 spectra were acquired. A mass accuracy ≤ 2 ppm was obtained in the peak matching acquisition mode by using a solution containing 2 µl PEG200, 2 µl PPG450, and 1.5 mg NaOAc (all obtained from Sigma-Aldrich, CH-Buchs) dissolved in 100ml MeOH (HPLC Supra grade, *Scharlau*, E-

Barcelona) as internal standard. GC-MS analyses were done on a Finnigan Voyager GC8000 Top. Elemental analyses were done on a Leco CHN-932 analyzer. Optical rotations were measured at 25 ºC on a Jasco P-2000 Polarimeter using a filtered Hg lamp (λ = 589 nm). X-ray crystallography was performed on a *Nonius Kappa CCD* area-detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. Ligand SIPrNap•HBF_4[15] and catalysts[5c] ([(DiPhSIPrNap)Pd(cin)Cl] (**1a**), [(DiPhSI2PrNap)Pd(cin)Cl] (**1b**) and [(DiPhSI2CyNap)Pd(cin)Cl] (**1c**) were prepared according to literature procedures.

2-(3-Pentyl)-naphthalene. In a 100 mL 3-necked flask, equipped with a condenser, an addition funnel and a N_2 inlet, were added magnesium turnings (0.59 g, 24.36 mmol) (and 1 crystal of I_2) and 20 mL THF under N_2 flow. In the addition funnel was charged 2-bromonaphthalene (4.80 g, 23.18 mmol) and 25 mL THF, and this solution was added slowly into the 3-necked flask at 60°C. At the end of the addition, the mixture was reflux for 1h. In a 250 mL schlenk flask was added 3-bromopentane (3.50 g, 23.18 mmol) and $(FeCl_3)_2(TMEDA)_3$ (0.39 g, 0.58 mmol) in 20 mL THF. The Grignard reagent was then added dropwise into the Schlenk flask at 0°C and stirred at room temperature for 2h. The reaction was quenched with 1 N HCl aqueous solution, and extracted with Et_2O. The product was isolated as a colorless oil by flash chromatography using n-hexane as eluent (3.21 g, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18-7.76 (m, 3H), 7.56 (s, 1H), 7.46-7.38 (m, 2H), 7.30 (dd, *J* = 8.4, 1.5 Hz, 1H), 2.52-2.46 (m, 1H), 1.81-1.73 (m, 2H), 1.70-1.61 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.42, 133.81, 132.49, 128.02, 127.80, 127.74, 126.71, 126.28, 125.92, 125.18, 50.09, 29.47, 12.49. HRMS (EI) m/z calculated for $C_{15}H_{18}$ $[M]^+$ 198.1409, observed 198.1407.

1-Bromo-2-(3-Pentyl)-naphthalene. 2-(3-Pentyl)-naphthalene (5.00 g, 25.21 mmol) was dissolved in 150 mL CH_2Cl_2, and then a 50 mL CH_2Cl_2 solution of Br_2 (4.03 g, 25.21 mmol) was added dropwise over 2h at -78°C. After 24h at the same temperature, the reaction was finished (confirmed by GC-MS). The reaction was quenched by adding 100 mL of an aqueous solution of NaOH. The CH_2Cl_2 phase was separated and washed with 200 mL water, 200 mL 5% Na_2CO_3, dried by $MgSO_4$, filtered and purified by flash chromatography (n-hexane as eluent) to afford a light yellow oil (6.44 g, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (d, *J* = 8.6 Hz, 1H),

7.82-7.77 (m, 2H), 7.59 (dt, *J* = 6.8, 1.3 Hz, 1H), 7.49 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 3.54-3.47 (m, 1H), 1.86-1.77 (m, 2H), 1.70-1.63 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.89, 133.52, 132.79, 128.22, 128.15, 127.96, 127.35, 126.00, 125.63, 125.07. HRMS (EI) m/z calculated for $C_{15}H_{17}Br$ $[M]^+$ 276.0514, observed 276.0509.

1*S*,2*S*-N,N′-Bis[2-(3-pentyl)-naphthalen-1-yl]-1,2-diphenylethane-1,2-diamine. A 500 mL schlenk flask was charged with $Pd(dba)_2$ (0.51 g, 0.88 mmol), (±)-BINAP (0.67 g, 1.07 mmol), NaO^tBu (2.54 g, 26.46 mmol) and toluene (240 mL) and stirred for 20 min. 1-Bromo-2-(3-pentyl)-naphthalene (5.62 g, 20.28 mmol) and (*1S,2S*)-(-)-1,2-diphenylethylenediamine (1.87 g, 8.82 mmol) were then added and the reaction mixture was heated to 120 °C for 48 h. After cooling to room temperature, the resulting mixture was filtered through a celite filter and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by flash chromatography (SiO_2, 1:3 CH_2Cl_2/*n*-hexane) to afford 1*S*,2*S*-N,N′-bis[2-(3-pentyl)-naphthalen-1-yl]-1,2-diphenylethane-1,2-diamine as a white solid (3.04 g, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.68 (d, *J* = 6.8 Hz, 2H), 7.78 (d, *J* = 6.8 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.45-7.39 (m, 4H), 7.23 (d, *J* = 8.6, 2H), 7.01-6.95 (m, 10H), 5.09 (br s, 2H), 5.01 (br s, 2H), 2.90-2.83 (m, 2H), 1.88-1.81 (m, 2H), 1.55-1.45 (m, 4H), 1.04-0.98 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 6H), 0.52 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.01, 140.51, 136.00, 133.39, 130.12, 128.74, 128.27, 128.12, 127.24, 125.22, 124.97, 124.79, 124.78, 124.23, 69.03, 42.24, 28.97, 28.55, 12.67, 12.09. HRMS (ESI) m/z calculated for $C_{44}H_{48}N_2Na$ $[M+Na]^+$ 627.3710, observed 627.3714.

***4S,5S-1*,3-Bis[2-(3-pentyl)-naphthalen-1-yl]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (DiPhSI2(3-Pen)Nap·HBF$_4$)**. Diamine 1*S*,2*S*-N,N′-bis[2-(3-pentyl)-naphthalen-1-yl]-1,2-diphenylethane-1,2-diamine (1.80 g, 2.98 mmol), ammonium tetrafluoroborate (0.37 g, 3.57 mmol), triethyl orthoformate (4.96 mL, 29.80 mmol) and two drops of formic acid were heated to 120 °C and stirred for 16 h. The resulting mixture was dried *in vacuo*, and the residue was purified by flash chromatography (SiO_2, 1:20 methanol:methylene chloride) to afford the product as an off-white foam (1.75 g, 84%). $[\alpha]^{27}_D$ = -113.84 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) exists as a mixture of three atropisomers (41:41:18): δ 8.31-7.16 (m, NC*H*N and Ar*H*) (correspond to the three atropisomers of twenty three protons), {6.71 (s, NC*H*Ph), 6.57 (d, *J* = 12.0 Hz, NC*H*Ph), 6.23 (s, NC*H*Ph), 6.22 (d, *J* = 12.8 Hz,

NC*H*Ph) (correspond to the three atropisomers of two protons)}, 3.66-0.20 (m, *3-Pentyl*) (correspond to the three atropisomers of twenty two protons)}. ^{13}C NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C NMR spectrum appeared complex): δ 159.37, 158.74, 158.45, 144.81, 143.71, 142.43, 141.66, 133.17, 133.07, 132.78, 132.71, 132.55, 132.47, 132.27, 132.20, 131.36, 131.30, 131.24, 130.78, 130.71, 130.62, 130.49, 130.39, 130.20, 130.14, 130.10, 130.03, 129.87, 129.81, 129.69, 129.61, 129.37, 129.33, 129.23, 129.15, 128.63, 128.44, 128.18, 127.78, 127.56, 127.46, 127.17, 127.07, 127.05, 126.08, 124.89, 124.36, 124.26, 123.87, 122.28, 121.42, 121.08, 120.29, 76.08, 74.73, 73.63, 45.17, 44.84, 43.63, 43.16, 29.61, 28.94, 28.77, 28.62, 27.87, 27.78, 27.18, 27.12, 13.61, 13.46, 12.95, 12.73, 12.58, 12.28, 12.21, 11.95. HRMS (ESI) m/z calculated for $C_{45}H_{47}N_2$ $[M\text{-}BF_4]^+$ 615.3734, observed 615.3732.

Chloro[(1,2,3-n)-3-phenyl-2-propenyl][*4S*,*5S*-*1*,3-Bis[2-(3-pentyl)-naphthalen-1-yl]-4,5-di-(4-methoxyl-phenyl)-4,5-dihydro-imidazol-2-ylidene] palladium(II) [(DiPhSI2(3-Pen)Nap)Pd(cin)Cl] (**1d**). DiPhSI2(3-Pen)Nap·HBF_4 (1.07 g, 1.52 mmol), KO^{t}Bu (0.17 g, 1.52 mmol) and $[Pd(cin)Cl]_2$ (0.38 g, 0.73 mmol) were mixed together in a round flask in the glovebox. Dry THF (20 mL) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo*, and the residue was separated by first flash chromatography (SiO_2, 1:6→1:3 EtOAc/*n*-hexane) to afford three pure atropisomers (1.04 g, 82%). Elemental analysis (%) calculated for $C_{54}H_{55}PdN_2Cl$: C, 74.21; H, 6.34; N, 3.20. Found: C, 74.39; H, 6.51; N, 3.08. HRMS (ESI) m/z calculated for $^{12}C_{54}H_{55}{}^{104}Pd^{14}N_2$ $[M\text{-}Cl]^+$ 837.3413, observed 837.3407.

Data for ***R*$_a$,*S*$_a$-1d** are as follows (first spot). (0.40 g, 32%). $[\alpha]^{28}_D$ = -274.05 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.47 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 7.92-6.96 (br m, 25H), 6.11 (br d, *J* = 8.8 Hz, 1H), 5.67 (d, *J* = 9.2 Hz, 1H), 4.62-3.00 (br m, 4H), 2.51-0.24 (br m, 22H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.40, 163.32, 145.68, 143.91, 138.30, 138.15, 137.85, 137.17, 133.58, 133.06, 132.98, 132.64, 131.88, 130.94, 129.22, 129.19, 128.98, 128.89, 128.68, 128.61, 128.47, 128.11, 128.09, 127.97, 127.40, 127.21, 126.69, 126.55, 126.49, 126.37, 125.98, 125.51, 125.07, 124.74, 124.67, 124.05, 121.30, 109.59, 106.05, 88.74, 88.28, 81.94, 59.56, 50.24, 49.44, 42.64, 41.47, 40.11, 34.29, 32.09, 29.87, 29.83, 29.53, 29.27,

28.65, 28.04, 27.85, 27.62, 26.92, 22.86, 22.50, 14.58, 14.30, 14.24, 12.35, 11.94, 11.74, 11.64.

Data for ***S*$_a$,*S*$_a$-1d** are as follows (second spot). (0.17 g, 13%). $[\alpha]^{28}_D$ = -193.27 (c = 0.4, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.58 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 7.9 Hz, 4H), 7.41-6.96 (m, 15H), 6.53 (d, *J* = 6.5 Hz, 2H), 5.75 (s, 2H), 3.69-3.43 (br m, 4H), 2.31-0.90 (br m, 22H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 216.87, 142.56, 139.01, 138.32, 133.42, 132.87, 131.81, 129.21, 128.96, 128.89, 128.13, 128.02, 127.96, 127.40, 127.36, 127.24, 126.43, 125.59, 125.52, 125.29, 109.58, 78.18, 49.54, 42.05, 28.76, 28.64, 14.25, 13.87, 12.09.

Data for ***R*$_a$,*R*$_a$-1d** are as follows (third spot). (0.47 g, 37%). $[\alpha]^{28}_D$ = -314.30 (c = 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (br s, 2H), 7.91-7.04 (br m, 25H), 6.08 (br s, 2H), 5.04 (br s, 0.6H), 4.62 (br s, 0.4H), 4.23 (d, *J* = 12.1 Hz, 1H), 3.26 (br s, 2H), 2.44-0.28 (br m, 22H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.39, 144.82, 137.43, 135.83, 133.17, 131.27, 129.20, 128.96, 128.68, 128.34, 127.35, 126.86, 128.34, 127.35, 126.86, 126.38, 125.95, 125.60, 108.82, 92.49, 89.91, 74.75, 47.58, 40.81, 32.09, 29.87, 29.83, 29.53, 27.73, 26.00, 22.86, 22.50, 14.29, 14.23, 12.62, 11.44.

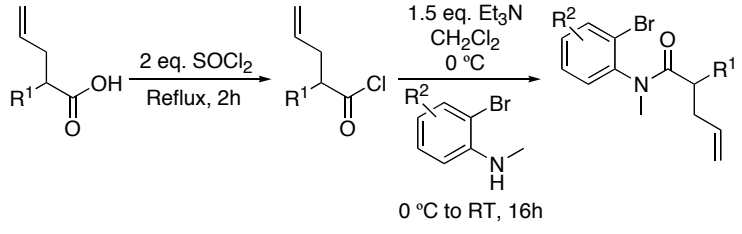
4.5.3 Synthesis of the substrates:[5a]

4.5.3.1 General procedure for the synthesis of 2-allyl-arylacetic acids

LDA was freshly prepared by adding a 2.5 M n-BuLi (2.1 eq.) solution in hexanes into 2.1 eq. diisopropylamine in THF at 0 ºC. The LDA solution was then cooled to –78 ºC, and 1.0 eq. arylacetic acid was added. After 1h, 2.1 eq. of ally bromide was added, and the reaction mixture was warmed to rt and kept for 2h. The reaction was quenched by 2N HCl aqueous solution, extracted with EtOAc, dried over $MgSO_4$, and concentrated to obtain the desired acid.

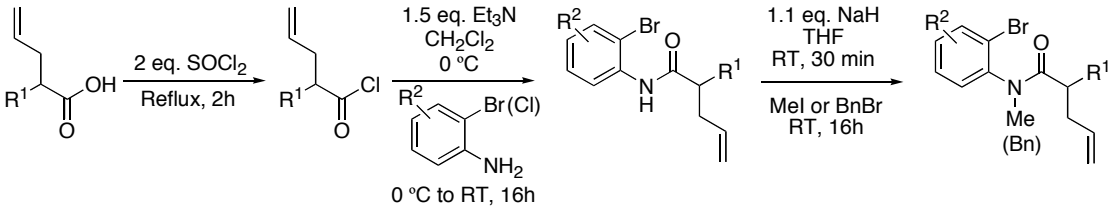
4.5.3.2 General procedure for the synthesis of substrates

***Method A**:*



The 2-allyl-arylacetic acid (1.0 eq.) was refluxed with $SOCl_2$ (2.0 eq.) for 2 h. The excess $SOCl_2$ was distilled out, 1.5 eq. Et_3N in CH_2Cl_2 was added at 0 ºC followed by the desired substituted *N*-methylaniline (1.0 eq.), and the resulting mixture was stirred for 16 h. The reaction was then quenched by an aqueous solution of NH_4Cl, extracted by CH_2Cl_2, dried over $MgSO_4$ and purified by flash chromatography to afford the corresponding substrate.

***Method B**:*



The 2-allyl-arylacetic acid (1.0 eq.) was refluxed with $SOCl_2$ (2.0 eq.) for 2 h. The excess $SOCl_2$ was distilled out, 1.5 eq. Et_3N in CH_2Cl_2 was added at 0 ºC followed by the desired substituted aniline (1.0 eq.), and the resulting mixture was stirred for 16 h. The reaction was then quenched by an aqueous solution of NH_4Cl, extracted by CH_2Cl_2, dried over $MgSO_4$ and purified by flash chromatography to afford the corresponding amide.

To a solution of the corresponding amide (1.0 equiv) in THF, 1.1 eq. NaH (60% in mineral oil) was added in small portions at RT, and the resulting mixture was stirred for 30 min. Subsequently, 1.1 MeI (or BnBr) in THF was added dropwise at 0 °C, and the resulting mixture was stirred overnight at RT. The reaction mixture was then filtered through a pad of silica/celite, washed by CH_2Cl_2, and dried in *vacuo*. The residue was then purified by flash chromatography to afford the corresponding substrate.

***N*-(2-Bromophenyl)-*N*-methyl-2-phenyl-pent-4-enamide (2a) (Route B)**. Isolated as a colorless oil (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.54 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.43-7.08 (m, 5.3H), 6.95-6.89 (m, 1H), 6.58 (dd, *J* = 7.8, 1.7 Hz, 0.7H), 5.67-5.57 (m, 1H), 5.01-4.86 (m, 2H), 3.40 (t, *J* = 7.0 Hz, 0.3H), 3.17 (t, *J* = 7.0 Hz, 0.7H), 3.16 (s, 0.9H), 3.14 (s, 2.1H), 2.85-2.77 (m, 1H), 2.45-2.35 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.66, 172.60, 142.58, 142.24, 139.72, 138.79, 136.46, 136.26, 134.20, 133.80, 131.29, 130.81, 129.93, 128.77, 128.62, 128.54, 128.51, 128.41, 128.23, 127.11, 127.06, 124.61, 123.69, 116.85,

116.64, 50.61, 49.59, 39.63, 39.39, 36.35, 36.31. HRMS (EI) m/z calculated for $C_{18}H_{18}BrNO$ $[M]^+$ 343.0572, observed 343.0562.

***N*-(2-Bromophenyl)-*N*-methyl-2-(1-naphthyl)-pent-4-enamide (2b) (Route B)**. Isolated as a colorless oil (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.53 (m, 4H), 7.40-7.29 (m, 2.7H), 7.14-7.09 (m, 2.2H), 6.85 (dt, *J* = 7.6, 1.6 Hz, 0.7H), 6.39 (dt, *J* = 7.7, 1.4 Hz, 0.7H), 5.98 (dd, *J* = 7.8, 1.6 Hz, 0.7H), 5.82-5.68 (m, 1H), 5.07-4.88 (m, 2H), 4.37 (dd, *J* = 8.6, 6.2 Hz, 0.3H), 4.05 (dd, *J* = 8.6, 6.2 Hz, 0.7H), 3.18 (s, 0.9H), 3.16 (s, 2.1H), 3.03-2.93 (m, 1H), 2.48-2.39 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.92, 172.75, 142.28, 141.67, 136.78, 136.67, 136.57, 134.94, 134.20, 133.90, 133.79, 133.45, 131.42, 131.03, 130.78, 130.51, 129.59, 129.44, 128.81, 128.77, 128.69, 128.21, 127.48, 126.10, 125.95, 125.84, 125.70, 125.67, 125.40, 125.09, 124.96, 124.43, 123.30, 122.24, 122.07, 116.66, 116.45, 45.53, 39.60, 39.35, 36.31, 36.29. HRMS (EI) m/z calculated for $C_{22}H_{20}BrNO$ $[M]^+$ 393.0728, observed 393.0727.

***N*-(2-Bromophenyl)-*N*-methyl-2-(2-naphthyl)-pent-4-enamide (2c) (Route B)**. Isolated as a colorless oil (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.64 (m, 3.7H), 7.51-7.18 (m, 5.2H), 7.10 (dd, *J* = 8.5, 1.7 Hz, 0.7H), 7.02 (dt, *J* = 7.7, 1.4 Hz, 0.7H), 6.50(dd, *J* = 7.8, 1.6 Hz, 0.7H), 5.71-5.60 (m, 1H), 5.04-4.87 (m, 2H), 3.60 (t, *J* = 7.5 Hz, 0.3H), 3.36 (t, *J* = 7.5 Hz, 0.7H), 3.18 (s, 0.9H), 3.16 (s, 2.1H), 2.94-2.87 (m, 1H), 2.56-2.47 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.54, 172.48, 142.56, 142.16, 137.14, 136.36, 136.16, 134.13, 133.83, 133.53, 133.51, 132.79, 132.67, 131.37, 130.78, 129.97, 129.95, 128.82, 128.43, 138.22, 128.04, 127.93, 127.76, 127.71, 127.63, 127.01, 126.61, 126.40, 126.14, 125.91, 125.84, 125.66, 124.69, 123.69, 116.93, 116.75, 50.74, 49.71, 39.53, 39.2126.34, 36.31. HRMS (EI) m/z calculated for $C_{22}H_{20}BrNO$ $[M]^+$ 393.0728, observed 393.0727.

***N*-Benzyl-*N*-(2-bromophenyl)-2-phenyl-pent-4-enamide (2d) (Route B)**. Isolated as a colorless oil (79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.0, 1.3 Hz, 0.7H), 7.57-7.55 (m, 0.3H), 7.26-6.98 (m, 10H), 6.92-6.85 (m, 2H), 6.80-6.78 (m, 0.3H), 6.20 (dd, *J* = 7.8, 1.6 Hz, 0.7H), 5.80-5.58 (m, 2H), 5.27-4.89 (m, 2H), 3.98 (d, *J* = 14.4 Hz, 0.7H), 3.84 (d, *J* = 14.4 Hz, 0.3H), 3.37 (dd, *J* = 8.5, 6.5 Hz, 0.3H), 3.19 (t, *J* = 7.4 Hz, 0.7H), 2.91-2.83 (m, 1H), 2.48-2.40 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.51, 172.43, 140.35, 140.11, 139.63, 138.71, 137.32, 137.20, 136.46, 136.03, 134.07, 133.64, 132.71, 132.59, 129.94, 129.89, 129.44, 129.22, 128.67,

128.50, 128.42, 128.16, 128.07, 127.75, 127.64, 127.51, 127.18, 1727.05, 124.89, 124.09, 1217.00, 116.67, 51.77, 51.56, 50.93, 49.59, 39.64. HRMS (EI) m/z calculated for $C_{24}H_{22}BrNO$ $[M]^+$ 419.0885, observed 419.0879.

***N*-(2-Bromophenyl)-*N*-methyl-2-*o*-tolyl-pent-4-enamide (2e) (Route B)**. Isolated as a colorless oil (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 8.0, 1.4 Hz, 0.8H), 7.48-7.46 (m, 0.2H), 7.39-7.32 (m, 1.2H), 7.18-6.87 (m, 5H), 6.25 (dd, *J* = 7.8, 1.7 Hz, 0.8H), 5.78-5.70 (m, 1H), 5.03-4.89 (m, 2H), 3.76 (dd, *J* = 8.8, 6.0 Hz, 0.2H), 3.40 (dd, *J* = 8.8, 6.0 Hz, 0.8H), 3.16 (s, 0.6H), 3.13 (s, 2.4H), 2.84-2.75 (m, 1H), 2.24-2.15 (m, 1H), 1.42 (s, 0.6H), 1.38 (s, 2.4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.82, 172.73, 142.53, 141.98, 138.74, 137.16, 136.77, 136.54, 135.67, 135.49, 134.32, 133.57, 131.02, 130.88, 130.17, 130.04, 129.70, 128.88, 128.53, 127.87, 126.82, 126.76, 126.55, 124.47, 123.90, 116.60, 116.39, 53.60, 46.46, 44.84, 39.42, 38.93, 36.30, 36.27, 18.60, 18.53. HRMS (EI) m/z calculated for $C_{19}H_{20}BrNO$ $[M]^+$ 357.0728, observed 357.0722.

***N*-(2-Bromophenyl)-*N*-methyl-2-(*o*-fluorophenyl)-pent-4-enamide (2f) (Route A)**. Isolated as a colorless oil (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.52-7.37 (m, 1.7H), 7.31-7.28 (m, 0.3H), 7.23-7.01 (m, 3.6H), 6.82-6.75 (m, 1H), 6.48 (dd, *J* = 7.8, 1.5 Hz, 0.7H), 5.69-5.58 (m, 1H), 5.00-4.86 (m, 2H), 3.89 (t, *J* = 7.3 Hz, 0.3H), 3.63 (t, *J* = 7.3 Hz, 0.7H), 3.17 (s, 0.9H), 3.15 (s, 2.1H), 2.81-2.75 (m, 1H), 2.41-2.31 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.20, 172.09, 161.58, 161.25, 159.14, 158.80, 142.11, 141.78, 135.81, 135.65, 134.13, 133.83, 130.55, 130.44, 129.95, 129.83, 129.80, 129.08, 129.04, 128.88, 128.63, 128.57, 128.54, 128.49, 127.07, 126.92, 125.97, 125.82, 124.54, 124.08, 123.58, 117.19, 116.95, 115.18, 115.02, 114.96, 114.79, 41.72, 41.70, 40.22, 40.20, 38.84, 38.57, 36.35, 36.32. HRMS (EI) m/z calculated for $C_{18}H_{17}BrNOF$ $[M]^+$ 361.0478, observed 361.0470.

***N*-(2-Bromophenyl)-*N*-methyl-2-(*o*-methoxylphenyl)-pent-4-enamide (2g) (Route B)**. Isolated as a colorless oil (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.47 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.45 (dd, *J* = 3.5, 1.3 Hz, 0.3H), 7.38-7.28 (m, 1.3H), 7.20-7.08 (m, 2H), 6.96 (dt, *J* = 7.7, 1.4 Hz, 0.7H), 6.89-6.85 (m, 1H), 6.61 (d, *J* = 8.2 Hz, 0.3H), 6.57 (d, *J* = 8.2 Hz, 0.7H), 6.38 (dd, *J* = 7.8, 1.6 Hz, 0.7H), 5.76-5.65 (m, 1H), 5.03-4.85 (m, 2H), 4.12 (dd, *J* = 8.7, 1.4 Hz, 0.3H), 3.80 (dd, *J* = 8.7, 1.4 Hz, 0.7H), 3.35 (s, 0.9H), 3.32 (s, 2.1H), 3.15 (s, 0.9H), 3.13 (s, 2.H), 2.82-

2.71 (m, 1H), 2.31-2.23 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.43, 173.39, 156.28, 156.11, 142.69, 142.17, 136.92, 136.63, 133.64, 133.45, 130.92, 130.89, 129.31, 129.26, 129.10, 128.60, 128.19, 128.05, 127.96, 127.88, 127.34, 124.41, 123.93, 120.84, 120.77, 116.43, 116.02, 109.84, 109.67, 54.91, 54.88, 41.84, 39.96, 38.96, 38.50, 36.27. HRMS (EI) m/z calculated for $C_{19}H_{20}BrNO_2$ $[M]^+$ 373.0677, observed 373.0674.

***N*-(2-Bromophenyl)-*N*-methyl-2-*m*-tolyl-pent-4-enamide (2h) (Route B)**. Isolated as a colorless oil (77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.52 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.40 (dt, *J* = 7.7, 1.4 Hz, 0.3H), 7.31 (dd, *J* = 7.8, 1.6 Hz, 0.3H), 7.24-7.16 (m, 1H), 7.11-7.00 (m, 1.7H), 6.97-6.93 (m, 1H), 6.72-6.64 (m, 2H), 6.57 (dd, *J* = 7.7, 1.6 Hz, 0.7H), 5.58-5.57 (m, 1H), 5.02-4.85 (m, 2H), 3.38 (dd, *J* = 8.8, 6.0 Hz, 0.3H), 3.13 (dd, *J* = 8.8, 6.0 Hz, 0.7H), 3.16 (s, 0.9H), 3.12 (s, 2.1H), 2.86-2.77 (m, 1H), 2.43-2.35 (m, 1H), 2.23 (s, 2.1H), 2.22 (s, 0.9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.60, 172.56, 142.49, 142.12, 139.51, 138.49, 138.01, 137.77, 136.50, 136.31, 134.03, 133.67, 131.38, 130.76, 129.82, 129.24, 128.78, 128.68, 128.28, 128.16, 127.72, 125.55, 125.25, 124.58, 123.61, 116.66, 116.45, 50.52, 49.49, 39.49, 39.11, 36.25, 36.22, 21.52, 21.50. HRMS (EI) m/z calculated for $C_{19}H_{20}BrNO$ $[M]^+$ 357.0728, observed 357.0724.

***N*-(2-Bromophenyl)-*N*-methyl-2-(*m*-fluorophenyl)-pent-4-enamide (2i) (Route B)**. Isolated as a colorless oil (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.56 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.44-7.39 (m, 0.3H), 7.32-7.10 (m, 3.4 H), 6.89-6.84 (m, 1H), 6.72-6.61 (m, 2.3H), 5.64-5.54 (m, 1H), 5.01-4.87 (m, 2H), 3.40 (t, *J* = 7.5 Hz, 0.3H), 3.19 (t, *J* = 7.5 Hz, 0.7H), 3.17 (s, 0.9H), 3.15 (s, 2.1H), 2.83-2.75 (m, 1H), 2.45-2.34 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.10, 172.02, 164.15, 164.09, 161.71, 161.66, 142.35, 142.17, 142.09, 142.05, 141.24, 141.16, 135.93, 135.74, 134.24, 133.91, 131.09, 130.70, 130.11, 129.96, 129.88, 129.76, 129.68, 128.88, 128.59, 124.44, 124.34, 124.31, 123.90, 123.87, 123.62, 117.19, 117.01, 115.64, 115.42, 115.25, 115.04, 114.12, 113.91, 50.26, 50.24, 49.26, 49.24, 39.48, 39.27, 36.37, 36.34. HRMS (EI) m/z calculated for $C_{18}H_{17}BrNOF$ $[M]^+$ 361.0478, observed 361.0468.

***N*-(2-Bromophenyl)-*N*-methyl-2-(*m*-methoxylphenyl)-pent-4-enamide (2j) (Route A)**. Isolated as a colorless oil (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.54 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.40 (dt, *J* = 7.6, 1.4 Hz, 0.3H), 7.31-

7.03 (m, 3H), 6.72-6.66 (m, 1H), 6.62 (dd, *J* = 7.7, 1.6 Hz, 0.7H), 6.51-6.47 (m, 2H), 5.67-5.57 (m, 1H), 5.02-4.86 (m, 2H), 3.70 (s, 0.9H), 3.69 (s, 2.1H), 3.38 (dd, *J* = 8.1, 6.9 Hz, 0.3H), 3.18 (s, 0.9H), 3.14 (dd, *J* = 8.1, 6.9 Hz, 0.7H), 3.13 (s, 2.1H), 2.84-2.76 (m, 1H), 2.44-2.34 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.45, 172.41, 159.74, 159.62, 142.53, 142.18, 141.21, 140.20, 136.42, 136.21, 134.13, 133.76, 131.35, 130.77, 129.91, 129.43, 139.27, 128.76, 128.47, 124.60, 123.65, 121.07, 120.61, 116.83, 116.61, 114.27, 113.88, 113.46, 113.00, 112.83, 55.31, 50.62, 49.59, 39.53, 39.24, 36.34, 36.30. HRMS (EI) m/z calculated for $C_{19}H_{20}BrNO_2$ $[M]^+$ 373.0677, observed 373.0662.

***N*-(2-Bromophenyl)-*N*-methyl-2-*p*-tolyl-pent-4-enamide (2k) (Route B)**. Isolated as a colorless oil (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.55 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.39 (dt, *J* = 7.7, 1.4 Hz, 0.3H), 7.32-7.10 (m, 2H), 6.99-6.96 (m, 2H), 6.62 (dd, *J* = 7.7, 1.6 Hz, 0.7H), 5.67-5.56 (m, 1H), 5.00-4.85 (m, 2H), 3.37 (dd, *J* = 8.8, 6.0 Hz, 0.3H), 3.11 (dd, *J* = 8.8, 6.0 Hz, 0.7H), 3.16 (s, 0.9H), 3.13 (s, 2.1H), 2.83-2.75 (m, 1H), 2.43-2.36 (m, 1H), 2.28 (s, 2.1H), 2.26 (s, 0.9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.83, 172.82, 142.63, 142.25, 136.59, 136.57, 136.54, 136.31, 135.74, 134.15, 133.74, 131.30, 130.76, 129.88, 129.21, 129.05, 128.73, 128.48, 128.45, 128.07, 124.53, 123.65, 116.75, 116.51, 50.08, 49.05, 39.62, 39.36, 36.28, 26.24, 21.24, 21.22. HRMS (EI) m/z calculated for $C_{19}H_{20}BrNO$ $[M]^+$ 357.0728, observed 357.0723.

***N*-(2-Bromophenyl)-*N*-methyl-2-(*p*-fluorophenyl)-pent-4-enamide (2l) (Route A)**. Isolated as a colorless oil (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.55 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.41 (dt, *J* = 8.7, 1.3 Hz, 0.3H), 7.32-7.19 (m, 1.6 H), 7.14 (dt, *J* = 7.7, 1.4 Hz, 0.7H), 6.93-6.82 (m, 4H), 6.60 (dd, *J* = 7.7, 1.6 Hz, 0.7H), 5.63-5.53 (m, 1H), 4.99-4.86 (m, 2H), 3.38 (t, *J* = 7.5 Hz, 0.3H), 3.18 (t, *J* = 7.5 Hz, 0.7H), 3.16 (s, 0.9H), 3.14 (s, 2.1H), 2.81-2.74 (m, 1H), 2.43-2.32 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.58, 172.51, 163.40, 163.26, 160.96, 160.82, 142.49, 142.17, 136.11, 135.91, 135.40, 135.36, 134.55, 134.52, 134.23, 133.92, 131.12, 130.76, 130.16, 130.08, 130.05, 129.77, 129.69, 128.87, 128.57, 124.48, 123.70, 117.09, 116.91, 115.48, 115.31, 115.27, 115.09, 49.71, 48.72, 39.63, 39.43, 36.35, 36.31. HRMS (EI) m/z calculated for $C_{18}H_{17}BrNOF$ $[M]^+$ 361.0478, observed 361.0474.

***N*-(2-Bromophenyl)-*N*-methyl-2-(*p*-methoxylphenyl)-pent-4-enamide (2m) (Route B)**. Isolated as a colorless oil (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.55 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.31-7.11 (m, 2H), 6.87-6.80 (m, 2H), 6.72-6.68 (m, 2H), 6.62 (dd, *J* = 7.7, 1.6 Hz, 0.7H), 5.65-5.55 (m, 1H), 4.99-4.84 (m, 2H), 3.74 (s, 2.1H), 3.72 (s, 0.9H), 3.34 (t, *J* = 7.5 Hz, 0.3H), 3.15 (s, 0.9H), 3.12 (s, 2.1H), (t, *J* = 7.5 Hz, 0.7H), 2.80-2.73 (m, 1H), 2.42-2.32 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.93, 172.89, 158.75, 158.66, 142.59, 142.23, 136.50, 136.27, 134.13, 133.74, 131.72, 131.26, 130.93, 130.74, 129.87, 129.57, 129.19, 128.73, 138.46, 124.54, 123.64, 116.74, 116.52, 113.87, 113.76, 55.35, 49.59, 48.58, 39.60, 39.37, 36.24, 36.19. HRMS (EI) m/z calculated for $C_{19}H_{20}BrNO_2$ $[M]^+$ 373.0677, observed 373.0673.

***N*-(2-Bromophenyl)-*N*-methyl-2-(*p*-trifluoromethylphenyl)-pent-4-enamide (2n) (Route B)**. Isolated as a colorless oil (79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.56 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.44-7.40 (m, 2.3H), 7.33-7.20 (m, 1.6H), 7.16-7.03 (m, 2.4H), 6.59 (dd, *J* = 7.7, 1.6 Hz, 0.7H), 5.63-5.52 (m, 1H), 5.00-4.88 (m, 2H), 3.46 (t, *J* = 7.5 Hz, 0.3H), 3.25 (t, *J* = 7.5 Hz, 0.7H), 3.16 (s, 0.9H), 3.15 (s, 2.1H), 2.85-2.77 (m, 1H), 2.46-2.35 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.92, 171.87, 143.69, 142.80, 142.34, 142.02, 135.67, 135.48, 134.29, 134.03, 130.97, 130.72, 130.20, 129.59, 129.27, 129.03, 128.98, 128.66, 128.59, 125.78, 125.70, 125.55, 125.51, 125.47, 125.44, 125.34, 125.30, 124.34, 123.67, 122.99, 117.44, 117.27, 50.36, 49.37, 39.49, 39.27, 36.42, 36.39. HRMS (EI) m/z calculated for $C_{19}H_{17}BrNOF_3$ $[M]^+$ 411.0446, observed 411.0440.

***N*-(2-Bromophenyl)-*N*-methyl-2-(*p*-biphenyl)-pent-4-enamide (2o) (Route B)**. Isolated as a white solid (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.57-7.53 (m, 2.6H), 7.44-7.20 (m, 7.3H), 7.14 (dt, *J* = 7.7, 1.3 Hz, 0.7H), 7.03 (d, *J* = 8.2 Hz, 0.6H), 7.00 (d, *J* = 8.2 Hz, 1.4H), 6.67 (dd, *J* = 7.8, 1.6 Hz, 0.7H), 5.72-5.61 (m, 1H), 5.05-4.90 (m, 2H), 3.46 (t, *J* = 7.5 Hz, 0.3H), 3.23 (t, *J* = 7.5 Hz, 0.7H), 3.19 (s, 0.9H), 3.17 (s, 2.1H), 2.89-2.82 (m, 1H), 2.51-2.41 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.63, 172.60, 142.57, 142.23, 141.19, 140.88, 139.95, 139.86, 138.74, 137.85, 136.38, 136.18, 134.23, 133.84, 131.31, 130.79, 129.97, 129.03, 128.95, 128.87, 128.79, 128.64, 128.56, 127.43, 127.27, 127.20, 127.12, 124.59, 123.68, 116.95, 116.75, 50.21, 49.22, 39.58, 39.27, 36.37, 36.34. HRMS (EI) m/z calculated for $C_{24}H_{22}BrNO$ $[M]^+$ 419.0885, observed 419.0882.

***N*-(2-Chlorophenyl)-*N*-methyl-2-(*o*-fluorophenyl)-pent-4-enamide (2p) (Route B)**. Isolated as a colorless oil (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.41 (m, 1.7H), 7.34-7.23 (m, 2H), 7.15-7.00 (m, 2.6H), 6.78 (t, *J* = 9.7 Hz, 1H), 6.51 (dd, *J* = 7.8, 1.5 Hz, 0.7H), 5.68-5.58 (m, 1H), 5.00-4.87 (m, 2H), 3.90 (t, *J* = 7.3 Hz, 0.3H), 3.64 (t, *J* = 7.3 Hz, 0.7H), 3.17 (s, 0.9H), 3.16 (s, 2.1H), 2.83-2.73 (m, 1H), 2.39-2.31 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.35, 172.22, 161.51, 161.24, 159.07, 158.79, 140.50, 140.29, 135.75, 135.69, 133.93, 133.02, 130.84, 130.65, 130.48, 130.39, 129.79, 129.76, 129.72, 129.69, 129.09, 129.05, 128.62, 128.54, 128.47, 128.17, 127.96, 127.09, 126.94, 125.94, 125.79, 124.54, 124.50, 124.42, 124.38, 117.14, 116.91, 115.19, 114.96, 114.94, 114.71, 41.52, 41.50, 40.37, 40.35, 38.70, 38.49, 36.34, 36.21. HRMS (EI) m/z calculated for $C_{18}H_{17}ClNOF$ $[M]^+$ 317.0983, observed 317.0981.

***N*-(2-Bromo-4-methoxyl-phenyl)-*N*-methyl-2-(*o*-fluorophenyl)-pent-4-enamide (2q) (Route A)**. Isolated as a white solid (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dt, *J* = 7.6, 1.8 Hz, 0.3H), 7.42 (dt, *J* = 7.6, 1.8 Hz, 0.7H), 7.19-7.01 (m, 3.3H), 6.90 (dd, *J* = 8.7, 1.8 Hz, 0.3H), 6.84-6.77 (m, 1H), 6.57 (dd, *J* = 8.7, 2.8 Hz, 0.7H), 6.36 (d, *J* = 8.7 Hz, 0.7H), 5.70-5.58 (m, 1H), 5.00-4.86 (m, 2H), 3.91 (t, *J* = 7.5 Hz, 0.3H), 3.80 (s, 0.9H), 3.78 (s, 2.1H), 3.66 (t, *J* = 7.5 Hz, 0.7H), 2.81-2.74 (m, 1H), 2.40-2.30 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.68, 172.67, 172.55, 172.53, 161.62, 161.30, 159.90, 159.86, 159.19, 158.86, 135.93, 135.74, 134.92, 134.58, 130.72, 130.65, 129.99, 129.84, 129.09, 129.05, 128.56, 128.50, 128.48, 128.42, 127.20, 127.05, 126.15, 126.00, 124.51, 124.48, 124.42, 124.38, 123.92, 118.84, 118.49, 117.13, 116.88, 115.19, 115.02, 114.97, 114.79, 114.63, 114.48, 55.98, 55.97, 41.54, 41.52, 40.03, 40.00, 38.91, 38.55, 36.55. HRMS (EI) m/z calculated for $C_{19}H_{19}BrNO_2F$ $[M]^+$ 391.0583, observed 391.0578.

***N*-(2-Bromo-4-methoxyl-phenyl)-*N*-methyl-2-methyl-pent-4-enamide (2r) (Route B)**. Isolated as a white solid (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.54 (m, 1H), 7.46-6.22 (m, 6H), 7.11-7.09 (m, 1H), 7.06-7.04 (m, 1.3H), 6.94 (dd, *J* = 8.7, 2.8 Hz, 0.3H), 6.66 (dd, *J* = 8.7, 2.8 Hz, 0.7H), 6.56 (d, *J* = 8.7 Hz, 0.7H), 5.73-5.63 (m, 1H), 5.06-4.90 (m, 2H), 3.83 (s, 0.9H), 3.81 (s, 2.1H), 3.50 (t, *J* = 7.5 Hz, 0.3H), 3.30 (t, *J* = 7.5 Hz, 0.7H), 3.17 (s, 0.9H), 3.14 (s, 2.1H), 2.95-2.85 (m, 1H), 2.47-2.40 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.02, 172.98, 159.84, 159.81, 141.13, 140.82, 139.82, 139.75, 138.79, 137.98, 136.42, 136.18, 135.26, 134.92, 1321.43, 130.91,

129.02, 128.88, 128.80, 128.63, 127.35, 127.20, 27.12, 127.10, 127.05, 127.01, 124.88, 123.97, 118.81, 118.52, 116.86, 116.63, 114.50, 114.17, 55.94, 55.92, 49.92, 48.96, 39.53, 39.30, 36.49. HRMS (EI) m/z calculated for $C_{25}H_{24}BrNO_2$ $[M]^+$ 449.0990, observed 449.0980.

***N*-(2-Bromo-3-methyl-phenyl)-*N*-methyl-2-(*o*-fluorophenyl)-pent-4-enamide (2s) (Route B)**. Isolated as a colorless oil (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.42 (m, 1H), 7.27-7.00 (m, 3.6H), 6.94 (t, *J* = 8.6 Hz, 0.7H), 6.77 (dt, *J* = 7.8, 1.3 Hz, 1H), 6.31 (d, *J* = 8.2 Hz, 0.7H), 5.69-5.58 (m, 1H), 5.00-4.85 (m, 2H), 3.87 (t, *J* = 7.5 Hz, 0.3H), 3.63 (t, *J* = 7.5 Hz, 0.7H), 3.17 (s, 0.9H), 3.14 (s, 2.1H), 2.81-2.74 (m, 1H), 2.47 (s, 2.1H), 2.42-2.33 (m, 1H), 2.31 (s, 0.9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.24, 172.07, 161.62, 161.26, 159.18, 158.81, 142.32, 142.01, 140.74, 140.44, 135.93, 135.71, 130.68, 130.57, 129.95, 129.92, 129.09, 129.05, 128.56, 128.48, 128.40, 128.06, 127.79, 127.62, 127.25, 127.10, 126.78, 126.10, 126.00, 125.96, 124.51, 124.48, 124.39, 124.36, 117.09, 116.87, 115.16, 114.94, 114.85, 114.62, 41.62, 41.60, 40.16, 40.14, 38.86, 38.64, 36.30, 36.25, 23.94, 23.77. HRMS (EI) m/z calculated for $C_{19}H_{19}BrNOF$ $[M]^+$ 375.0634, observed 375.0628.

***N*-(2-Bromophenyl)-*N*-methyl-2-(1-methyl-1*H*-indol-3-yl)-pent-4-enamide (2t) (Route B)**. Isolated as a colorless oil (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.44-7.35 (m, 0.9H), 7.24-7.10 (m, 3H), 7.03-6.88 (m, 3.7H), 6.60 (dd, *J* = 7.7, 1.6 Hz, 0.7H), 5.75-5.64 (m, 1H), 5.06-4.85 (m, 2H), 3.76 (t, *J* = 7.5 Hz, 0.3H), 3.71 (s, 2.1H), 3.69 (s, 0.9H), 3.52 (t, *J* = 7.5 Hz, 0.7H), 3.19 (s, 0.9H), 3.17 (s, 2.1H), 2.89-2.82 (m, 1H), 2.57-2.49 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.76, 173.53, 142.78, 142.48, 136.96, 136.75, 136.72, 134.09, 133.67, 130.86, 130.63, 129.70, 129.63, 128.65, 128.61, 127.72, 127.54, 127.42, 126.83, 124.31, 123.38, 121.53, 121.30, 119.12, 118.87, 118.84, 118.69, 116.45, 116.23, 112.98, 112.07, 109.15, 109.03, 41.04, 40.32, 39.72, 39.49, 36.16, 36.13, 32.86, 32.82. HRMS (EI) m/z calculated for $C_{21}H_{21}BrN_2O$ $[M]^+$ 396.0837, observed 396.0840.

***N*-(2-Bromo-4-methoxyl-phenyl)-*N*-methyl-2-methyl-pent-4-enamide (2u) (Route B)**. Isolated as a colorless oil (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.10 (m, 2H), 6.87-6.84 (m, 1H), 5.70-5.52 (m, 1H), 4.99-4.90 (m, 2H), 3.80 (s, 3H), 3.13 (s, 1.6H), 3.12 (s, 1.4H), 2.45-1.95 (m, 3H), 1.05 (d, *J* = 6.6 Hz, 1.6H), 0.97 (d, *J* = 6.6 Hz, 1.4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.87, 176.63, 159.76, 159.73, 136.67, 136.21, 135.70, 135.68, 130.79, 130.12, 124.07, 123.99, 118.94, 118.79, 116.78,

116.62, 114.70, 114.63, 55.97, 39.05, 38.26, 37.14, 36.99, 36.31, 36.28, 17.62. HRMS (EI) m/z calculated for $C_{14}H_{18}BrNO_2$ $[M]^+$ 311.0521, observed 311.0516.

***N*-(2-Bromophenyl)-*N*-methyl-2-(3,5-dimethylphenyl)-pent-4-enamide (2v) (Route A)**. Isolated as a colorless oil (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 8.0, 1.4 Hz, 0.7H), 7.53 (dd, *J* = 8.0, 1.4 Hz, 0.3H), 7.39 (dt, *J* = 7.6, 1.4 Hz, 0.3H), 7.29 (dd, *J* = 7.8, 1.7 Hz, 0.3H), 7.25-7.15 (m, 1H), 7.10 (dt, *J* = 7.7, 1.5 Hz, 0.7H), 6.79-6.77 (m, 1H), 6.59 (dd, *J* = 7.8, 1.6 Hz, 0.7H), 6.48 (s, 2H), 5.69-5.59 (m, 1H), 5.03-4.87 (m, 2H), 3.36 (t, *J* = 7.5 Hz, 0.3H), 3.17 (s, 0.9H), 3.14 (s, 2.1H), 3.09 (t, *J* = 7.5 Hz, 0.7H), 2.84-2.77 (m, 1H), 2.41-2.29 (m, 1H), 2.19 (s, 2.1H), 2.18 (s, 0.9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.73, 142.58, 142.19, 139.47, 138.34, 138.16, 137.86, 137.67, 136.71, 136.54, 134.01, 133.69, 131.63, 130.85, 129.81, 129.76, 128.67, 128.64, 128.14, 126.37, 126.01, 124.71, 123.69, 116.59, 116.39, 50.59, 49.53, 39.45, 38.93, 36.33, 36.30, 21.44, 21.42. HRMS (EI) m/z calculated for $C_{20}H_{22}BrNO$ $[M]^+$ 371.0885, observed 371.0883.

4.5.4 Pd-Catalyzed asymmetric intramolecular α-arylation to give oxindoles:

4.5.4.1 General procedure for catalytic reactions by using well-defined chiral palladium catalysts

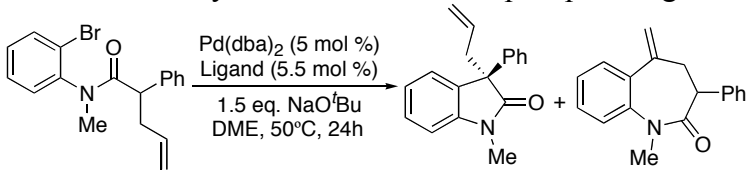
Catalyst (5 mol%) and base (1.5 eq.) were charged in a 20 mL vial in a glovebox. DME (2 mL) was added and the mixture was stirred for 5 min. The substrate (0.2 mmol, 1 eq.) was then added as a solution in 2 mL DME. The reaction was stirred at the indicated temperature, and monitored by GC-MS. After the required time, the reaction was treated with aq. NH_4Cl (10 mL) and this phase was extracted with 2×10 mL ether. The combined organic phases were washed with brine and dried over $MgSO_4$. Flash chromatography afforded the product oxindoles, and the enantiomeric purity of products was determined by chiral HPLC analysis.

4.5.4.2 General procedure for catalytic reactions by using chiral phosphine ligands

$Pd(dba)_2$ (5 mol%), chiral phosphine ligand (5.5 mol%) and base (1.5 eq.) were charged in a 20 mL vial in a glovebox. DME (2 mL) was added and the mixture was stirred for 5 min. The substrate **2a** (0.2 mmol, 1 eq.) was then added as a solution in 2 mL DME. The reaction was stirred at 50 ºC for 24h, and then the reaction was treated with aq. NH_4Cl (10 mL) and this aqueous phase was extracted with 2×10 mL ether. The combined organic phases were washed with brine and dried over $MgSO_4$. The conversions and the ratio **3a**/**4a** were determined by ^{1}H NMR of the crude

mixture. The enantiomeric purity of products was determined by chiral HPLC analysis.

Table S1. Catalytic results with chiral phosphine ligands.



2a **3a** **4a**

Entry	Ligand[a]	Conversion (%)[b]	**3a**/**4a**[c]	ee (%)[d]
1	(*S*)-BINAP	48	5:1	-29 (*S*)
2	(*S*)-BIPHEMP	50	6:1	-24 (*S*)
3	(*R*)-MeO-MOP	>99	5:1	0

[a] (*S*)-BINAP: (*S*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene; (*S*)-BIPHEMP: (*S*)-(6,6′-dimethyl-1,1′-biphenyl-2,2′-diyl)bis(diphenylphosphine); (*R*)-MeO-MOP: (*R*)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthalene. [b-c] Determined by analysis of ^{1}H NMR spectra of product mixtures prior to purification. [d] Determined by chiral HPLC for **3a**.

4.5.4.3 General procedure for preparing authentic racemic samples for HPLC analyses

$Pd(dba)_2$ (5 mol%), SIPrNap•HBF_4 (5.5 mol%) and base (1.5 eq.) were charged in a 20 mL vial in a glovebox. DME (2 mL) was added and the mixture was stirred for 5 min. The substrate (0.2 mmol, 1 eq.) was then added as a solution in 2 mL DME. The reaction was stirred at 50 ºC for 16h, and then the reaction was treated with aq. NH_4Cl (10 mL) and extracted with 2×10 mL ether. The combined organic phases were washed with brine and dried over $MgSO_4$. Flash chromatography afforded the product oxindoles, and the enantiomeric purity of products was determined by chiral HPLC analysis.

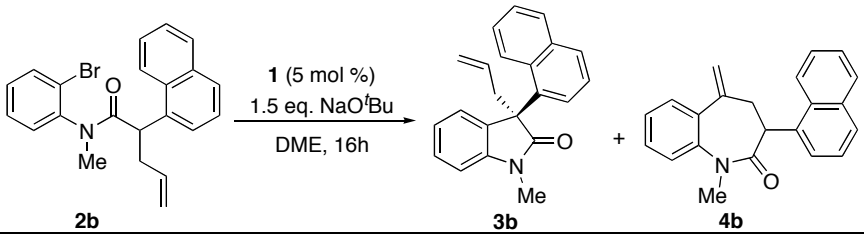
(*R*)-3-Allyl-1-methyl-3-phenyl-1,3-dihydro-indol-2-one (3a).[4a] Colorless oil, 96% yield. $[\alpha]^{27}_D$ = 118.26 (c = 1, $CHCl_3$), 81% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 99:1, 0.5 mL/min, t_R = 25.09 min (minor) and 26.16 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.20 (m, 7H), 7.10 (dt, *J* = 7.6, 1.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.43-5.33 (m, 1H), 5.04-4.89 (m, 2H), 3.19 (s, 3H), 3.01 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.18, 144.06, 139.72, 132.63, 131.89, 128.73, 128.42, 127.53, 125.39, 122.65, 119.34, 108.39, 56.60, 42.20, 26.55. HRMS (EI) m/z calculated for $C_{18}H_{17}NO$ $[M]^+$ 263.1310, observed 263.1309.

(±)-1-Methyl-5-methylidene-3-phenyl-1,3,4,5-tetrahydro-2*H*-1-benzazepin-2-one (4a). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.36 (m, 1H), 7.31-7.18 (m, 8H), 5.28-5.25 (m, 1H), 5.10-5.09 (m, 1H), 3.97 (dd, *J* = 13.1, 6.0 Hz, 1H), 3.36-3.29

(m, 1H), 3.31 (s, 3H), 3.14-3.04 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.00, 145.02, 142.25, 138.47, 137.40, 129.48, 129.07, 129.03, 128.33, 127.34, 126.58, 122.96, 116.07, 47.24, 44.44, 36.31. HRMS (EI) m/z calculated for $C_{18}H_{17}NO$ $[M]^+$ 263.1310, observed 263.1309.

(*R*)-3-Allyl-1-methyl-3-(1-naphthyl)-indolin-2-one (3b). Colorless oil, 98% yield. $[\alpha]^{27}_D$ = -17.02 (c = 0.5, $CHCl_3$), 87% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 95:5, 1 mL/min, t_R = 13.55 min (minor) and 27.96 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 9.3 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.32-7.27 (m, 2H), 7.15-7.11 (m, 1H), 7.03-6.91 (m, 3H), 6.82 (d, *J* = 7.3 Hz, 1H), 5.39-5.29 (m, 1H), 5.04-4.92 (m, 2H), 3.35 (s, 3H), 3.22-3.12 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.99, 143.43, 135.22, 134.72, 134.42, 131.79, 129.36, 128.30, 126.47, 126.32, 125.48, 125.25, 123.73, 123.61, 123.21, 119.72, 108.37, 56.60, 43.47, 26.53. HRMS (EI) m/z calculated for $C_{22}H_{19}NO$ $[M]^+$ 313.1467, observed 313.1461.

Table S2. Asymmetric intramolecular α-arylation of amide **2b** with **1a-d**.



2b **3b** **4b**

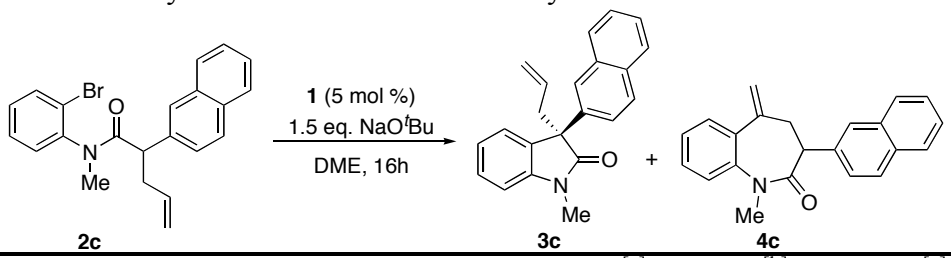
Entry	NHC•Pd	*T* (°C)	Conversion (%)[a]	**3b**/**4b**[b]	ee (%)[c]
1	R_a,R_a-**1a**	50	>99	10:1	-21 (*S*)
2	R_a,S_a-**1a**	50	>99	8:1	-14 (*S*)
3	S_a,S_a-**1a**	50	>99	9:1	10 (*R*)
4	R_a,R_a-**1b**	50	>99	9:1	33 (*R*)
5	R_a,S_a-**1b**	50	>99	6:1	10 (*R*)
6	R_a,R_a-**1c**	50	>99	8:1	59 (*R*)
7	R_a,S_a-**1c**	50	>99	6:1	32 (*R*)
8	R_a,R_a-**1d**	23	>99	1:0	87 (*R*)
9	R_a,S_a-**1d**	23	>99	17:1	39 (*R*)
10	S_a,S_a-**1d**	23	>99	19:1	53 (*R*)

[a-b] Determined by analysis of ^{1}H NMR spectra of product mixtures prior to purification.
[c] Determined by chiral HPLC for **3b**.

(*R*)-3-Allyl-1-methyl-3-(2-naphthyl)-indolin-2-one (3c). Colorless oil, 94% yield. $[\alpha]^{27}_D$ = 126.80 (c = 0.5, $CHCl_3$), 85% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, t_R = 16.07 min (minor) and 17.39 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.52 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.44-7.40 (m, 2H), 7.35 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.30 (d, *J* = 7.9Hz, 1H), 7.13 (dt, *J* = 8.0, 1.2 Hz, 1H),

6.91 (d, J = 7.9Hz, 1H), 5.48-5.38 (m, 1H), 5.08-4.91 (m, 2H), 3.22 (s, 3H), 3.13 (d, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.16, 144.14, 137.15, 133.42, 132.79, 132.6, 132.00, 128.53, 127.65, 126.27, 126.26, 126.13, 125.47, 125.36, 122.76, 119.45, 108.49, 56.74, 42.08, 26.60. HRMS (EI) m/z calculated for $C_{22}H_{19}NO$ $[M]^+$ 313.1467, observed 313.1461.

Table S3. Asymmetric intramolecular α-arylation of amide **2c** with **1a-d**.



2c **3c** **4c**

Entry	NHC•Pd	T (°C)	Conversion (%)[a]	**3c**/**4c**[b]	ee (%)[c]
1	R_a,R_a-**1a**	50	>99	7:1	-21 (*S*)
2	R_a,S_a-**1a**	50	>99	5:1	55 (*R*)
3	S_a,S_a-**1a**	50	>99	6:1	33 (*R*)
4	R_a,R_a-**1b**	50	>99	6:1	31 (*R*)
5	R_a,S_a-**1b**	50	>99	5:1	57 (*R*)
6	R_a,R_a-**1c**	50	>99	7:1	42 (*R*)
7	R_a,S_a-**1c**	50	>99	6:1	69 (*R*)
8	R_a,R_a-**1d**	23	>99	1:0	82 (*R*)
9	R_a,S_a-**1d**	23	>99	18:1	85 (*R*)
10	S_a,S_a-**1d**	23	>99	1:0	56 (*R*)

[a-b] Determined by analysis of ^{1}H NMR spectra of product mixtures prior to purification.
[c] Determined by chiral HPLC for **3c**.

(*R*)-3-Allyl-1-benzyl-3-phenylindolin-2-one (3d).[4a] Colorless oil, 89% yield. $[\alpha]^{27}_D$ = 87.29 (c = 0.5, $CHCl_3$), 81% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 97:3, 1 mL/min, t_R = 7.84 min (minor) and 8.42 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.17 (m, 12H), 7.06 (dt, J = 7.6, 1.0 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 5.47-5.36 (m, 1H), 5.10-4.81 (m, 4H), 3.16-3.03 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.27, 143.21, 139.96, 136.11, 132.70, 131.99, 128.87, 128.82, 128.33, 127.74, 127.60, 127.57, 127.24, 125.36, 122.72, 119.61, 109.53, 5.62, 44.14, 42.16. HRMS (EI) m/z calculated for $C_{14}H_{21}NO$ $[M]^+$ 339.1623, observed 339.1620.

Note: the absolute stereochemistry of compound 3d was assigned by comparison of both optical rotation and HPLC analysis (AD-H chiral column) with the know enantiomer.[10]

(*R*)-3-Allyl-1-methyl-3-*o*-tolylindolin-2-one (3e).[4a] White solid, 98% yield. $[\alpha]^{27}_D$ = -78.83 (c = 1, $CHCl_3$), 85% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 98:2, 1

mL/min, t_R = 10.69 min (minor) and 14.63 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.28-7.26 (m, 2H), 7.17 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.98 (dt, *J* = 7.6, 10.8 Hz, 1H), 6.86-6.83 (m, 2H), 5.35-5.25 (m, 1H), 5.00-4.87 (m, 2H), 3.24 (s, 3H), 3.09-2.99 (m, 2H), 1.62 (2, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.45, 144.14, 138.04, 137.32, 132.75, 132.19, 131.83, 128.15, 127.76, 127.53, 126.19, 123.55, 123.06, 119.52, 107.83, 56.44, 42.60, 26.30, 19.62. HRMS (EI) m/z calculated for $C_{19}H_{19}NO$ $[M]^+$ 277.1467, observed 277.1467.

(*S*)-3-Allyl-3-(2-fluorophenyl)-1-methylindolin-2-one (3f). Colorless oil, 94% yield. $[\alpha]^{27}_D$ = -111.08 (c = 1, $CHCl_3$), 91% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 98:2, 1 mL/min, t_R = 14.69 min (major) and 16.87 min (minor)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.28-7.20 (m, 2H), 7.03-6.88 (m, 3H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.39-5.27 (m, 1H), 5.05-4.90 (m, 2H), 3.26 (s, 3H), 3.10-3.00 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.98, 162.13, 159.66, 144.03, 132.43, 131.47, 129.44, 129.36, 128.53, 128.49, 128.34, 124.42, 124.38, 123.55, 123.53, 122.82, 119.79, 116.45, 116.22, 108.06, 53.7, 40.22, 26.51. HRMS (EI) m/z calculated for $C_{18}H_{16}NOF$ $[M]^+$ 281.1216, observed 281.1216.

(*S*)-3-Allyl-3-(2-methoxyphenyl)-1-methylindolin-2-one (3g).[4a] Colorless oil, 94% yield. $[\alpha]^{27}_D$ = -86.76 (c = 1, $CHCl_3$), 83% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 95:5, 1 mL/min, t_R = 11.34 min (minor) and 15.50 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.25-7.18 (m, 2H), 7.01 (dt, *J* = 7.7, 1.1 Hz, 1H), 6.91 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.85 (dd, *J* = 7.3, 1.0 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.74 (dd *J* = 8.2, 1.0 Hz, 1H), 5.39-5.27 (m, 1H), 5.00-4.86 (m, 2H), 3.39 (s, 3H), 3.25 (s, 3H), 2.98 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.43, 157.37, 144.62, 133.48, 131.95, 129.90, 128.85, 127.73, 127.64, 122.78, 122.28, 121.11, 119.22, 112.53, 107.22, 56.12, 53.96, 40.73, 26.35. HRMS (EI) m/z calculated for $C_{19}H_{19}NO_2$ $[M]^+$ 293.1416, observed 293.1415.

(*R*)-3-Allyl-1-methyl-3-*m*-tolylindolin-2-one (3h).[4a] Colorless oil, 91% yield. $[\alpha]^{26}_D$ = -120.39 (c = 1, $CHCl_3$), 83% ee [Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 95:5, 1 mL/min, t_R = 8.70 min (minor) and 22.44 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.18-7.03 (m, 5H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.42-5.32 (m, 1H), 5.03-4.88 (m, 2H), 3.19 (s, 3H), 3.00 (d, *J* = 7.1 Hz, 2H), 2.29 (2, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.28, 144.05, 139.69, 138.35, 132.72, 132.12, 128.59, 128.35, 127.87, 125.33, 124.28, 122.65,

119.27, 108.35, 56.58, 42.13, 26.55, 21.81. HRMS (EI) m/z calculated for $C_{19}H_{19}NO$ $[M]^+$ 277.1467, observed 277.1467.

(*R*)-3-Allyl-3-(3-fluorophenyl)-1-methylindolin-2-one (3i). Colorless oil, 97% yield. $[\alpha]^{26}_D$ = 126.19 (c = 1, $CHCl_3$), 85% ee [Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 95:5, 1 mL/min, t_R = 9.13 min (minor) and 13.73 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.27-7.06 (m, 5H), 6.95-6.88 (m, 2H), 5.41-5.31 (m, 1H), 5.05-4.90 (m, 2H), 3.19 (s, 3H), 2.97 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.63, 164.28, 161.84, 144.00, 142.29, 142.22, 132.23, 131.28, 130.16, 130.08, 128.72, 125.37, 123.01, 122.98, 122.83, 119.68, 114.75, 114.60, 114.53, 114.39, 108.58, 56.36, 42.29, 26.61. HRMS (EI) m/z calculated for $C_{18}H_{16}NOF$ $[M]^+$ 281.1216, observed 281.1217.

(*R*)-3-Allyl-3-(3-methoxyphenyl)-1-methylindolin-2-one (3j). Colorless oil, 90% yield. $[\alpha]^{27}_D$ = 100.31 (c = 0.5, $CHCl_3$), 85% ee [Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.5 mL/min, t_R = 15.622 min (major) and 17.25 min (minor)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.25-7.22 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.96-6.93 (m, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.77 (dd, *J* = 8.1, 1.5 Hz, 1H), 5.43-5.32 (m, 1H), 5.03-4.88 (m, 2H), 3.75 (s, 3H), 3.18 (s, 3H), 2.99 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.04, 159.86, 144.03, 141.32, 132.65, 131.83, 129.65, 128.44, 125.39, 122.68, 119.69, 119.35, 113.76, 112.46, 108.40, 56.55, 55.41, 42.18, 26.56. HRMS (EI) m/z calculated for $C_{19}H_{19}NO_2$ $[M]^+$ 293.1416, observed 293.1413.

(*R*)-3-Allyl-1-methyl-3-*p*-tolylindolin-2-one (3k).[4a] Colorless oil, 94% yield. $[\alpha]^{27}_D$ = 109.14 (c = 1, $CHCl_3$), 82% ee [Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 99.3:0.7, 0.5 mL/min, t_R = 35.09 min (major) and 39.06 min (minor)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.26-7.22 (m, 3H), 7.11-7.07 (m, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.44-5.33 (m, 1H), 5.03-4.88 (m, 2H), 3.18 (s, 3H), 2.99 (d, *J* = 7.1 Hz, 2H), 2.28 (2, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.33, 144.07, 137.24, 136.74, 132.75, 132.08, 129.44, 128.34, 127.12, 125.33, 122.61, 119.25, 108.34, 56.31, 42.13, 26.52, 21.15. HRMS (EI) m/z calculated for $C_{19}H_{19}NO$ $[M]^+$ 277.1467, observed 277.1463.

(*R*)-3-Allyl-3-(4-fluorophenyl)-1-methylindolin-2-one (3l).[4a] Colorless oil, 94% yield. $[\alpha]^{27}_D$ = 141.88 (c = 1, $CHCl_3$), 83% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 98:2, 1 mL/min, t_R = 7.26 min (minor) and 8.05 min (major)]. ^{1}H NMR (400

MHz, $CDCl_3$): δ 7.36-7.30 (m, 3H), 7.24-7.22 (m, 1H), 7.11 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.98-6.94 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.41-5.30 (m, 1H), 5.03-4.89 (m, 2H), 3.18 (s, 3H), 2.96 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.04, 163.51, 161.06, 144.01, 135.41, 135.38, 132.37, 131.56, 129.07, 128.99, 128.61, 125.36, 122.5, 119.55, 115.61, 115.40, 108.55, 55.98, 42.50, 26.57. HRMS (EI) m/z calculated for $C_{18}H_{16}NOF$ $[M]^+$ 281.1216, observed 281.1216.

(*R*)-3-Allyl-3-(4-methoxyphenyl)-1-methylindolin-2-one (3m). Colorless oil, 92% yield. $[\alpha]^{27}_D$ = 128.36 (c = 1, $CHCl_3$), 77% ee [Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 99:1, 1 mL/min, t_R = 29.00 min (major) and 32.42 min (minor)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.23 (m, 4H), 7.09 (dt, *J* = 7.6, 1.0 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.83-6.80 (m, 2H), 5.43-5.32 (m, 1H), 5.03-4.88 (m, 2H), 3.75 (s, 3H), 3.17 (s, 3H), 2.97 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.46, 159.02, 144.07, 132.76, 132.05, 131.76, 128.39, 128.37, 125.37, 122.61, 119.25, 114.11, 108.38, 55.93, 55.47, 42.34, 26.53. HRMS (EI) m/z calculated for $C_{19}H_{19}NO_2$ $[M]^+$ 293.1416, observed 293.1412.

(*R*)-3-Allyl-1-methyl-3-(4-trifluorophenyl)-indolin-2-one (3n). Colorless oil, 97% yield. $[\alpha]^{27}_D$ = 124.51 (c = 0.5, $CHCl_3$), 86% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 98:2, 1 mL/min, t_R = 6.50 min (minor) and 7.62 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (m, 4H), 7.35 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.25-7.23 (m, 1H), 7.12 (dt, *J* = 7.6, 1 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.42-5.31 (m, 1H), 5.05-4.91 (m, 2H), 3.19 (s, 3H), 3.00 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.47, 144.04, 143.68, 132.03, 131.04, 129.99, 129.67, 128.88, 127.83, 125.72, 125.68, 125.65, 125.61, 125.41, 122.93, 119.90, 108.73, 56.56, 42.32, 26.67. HRMS (EI) m/z calculated for $C_{19}H_{16}NOF_3$ $[M]^+$ 331.1184, observed 331.1182.

(*R*)-3-Allyl-3-(4-biphenyl)-1-methylindolin-2-one (3o).[4a] White solid, 95% yield. $[\alpha]^{27}_D$ = 107.04 (c = 1, $CHCl_3$), 87% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 98:2, 1 mL/min, t_R = 11.00 min (minor) and 13.08 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.51 (m, 4H), 7.46-7.29 (m, 7H), 7.13 (dt, *J* = 7.5, 0.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 5.48-5.38 (m, 1H), 5.08-4.92 (m, 2H), 3.21 (s, 3H), 3.06 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.14, 144.07, 140.86, 140.45, 138.74, 132.58, 131.80, 128.93, 128.49, 127.68, 126.48, 127.46, 127.26, 125.40, 122.71, 119.43, 108.46, 56.42, 42.21, 26.58. HRMS (EI) m/z calculated for $C_{24}H_{21}NO$ $[M]^+$ 339.1623, observed 339.1622.

(*S*)-3-Allyl-3-(2-fluorophenyl)-5-methoxyl-1-methylindolin-2-one (3q). Colorless oil, 90% yield. $[\alpha]^{22}_D$ = -86.04 (c = 0.5, $CHCl_3$), 94% ee [Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95:5, 1 mL/min, t_R = 11.55 min (minor) and 13.53 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dt, *J* = 7.8, 1.7 Hz, 1H), 7.26-7.20 (m, 1H), 7.15 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.91 (ddd, *J* =11.6, 8.1, 1.3 Hz, 1H), 6.79-6.73 (m, 2H), 6.64 (d, *J* = 2.2 Hz, 1H), 5.42-5.30 (m, 1H), 5.06-4.90 (m, 2H), 3.71 (s, 3H), 3.23 (s, 3H), 3.05-3.02 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.61, 162.16, 159.70, 156.27, 137.67, 133.79, 131.49, 129.48, 129.39, 128.54, 128.50, 127.95, 127.82, 124.43, 124.40, 119.80, 116.48, 116.25, 112.29, 111.28, 111.26, 108.27, 55.94, 54.30, 40.26, 26.61. HRMS (EI) m/z calculated for $C_{19}H_{18}NOF$ $[M]^+$ 311.1322, observed 311.1318.

(*R*)-3-Allyl-3-(4-biphenyl)-1-methyl-5-methoxyl-indolin-2-one (3r). White solid, 90% yield. $[\alpha]^{22}_D$ = 131.88 (c = 0.5, $CHCl_3$), 86% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 95:5, 1 mL/min, t_R = 10.71 min (minor) and 12.72 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.49 (m, 4H), 7.45-7.38 (m, 4H), 7.33-7.29 (m, 1H), 6.90-6.79 (m, 3H), 5.48-5.37 (m, 1H), 5.08-4.92 (m, 2H), 3.80 (s, 3H), 3.18 (s, 3H), 3.00 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.85, 156.16, 140.91, 140.49, 138.73, 137.70, 133.23, 132.39, 128.59, 127.68, 127.51, 127.50, 127.29, 119.50, 112.91, 112.67, 108.69, 56.87, 56.06, 42.10, 26.69. HRMS (EI) m/z calculated for $C_{25}H_{23}NO_2$ $[M]^+$ 369.1729, observed 369.1724.

(*S*)-3-Allyl-3-(2-fluorophenyl)-1,4-dimethylindolin-2-one (3s). White solid, 95% yield. [HPLC condition: Chiralpak IB, 2:98 (iPrOH/n-Hexane), 1 ml/min. 12.45 (major), 20.76 (minor).] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dt, *J* = 7.8, 0.8 Hz, 1H), 7.26-7.15 (m, 3H), 7.12 (ddd, *J* = 11.4, 8.0, 1.4 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.39-5.19 (m, 1H), 5.06-4.86 (m, 2H), 3.24-3.19 (m, 2H), 3.23 (s, 3H), 1.92 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.91, 162.03, 159.56, 144.46, 134.04, 131.33, 129.39, 129.31, 129.18, 128.93, 128.89, 128.25, 127.31, 127.19, 125.15, 124.23, 124.19, 119.46, 116.34, 116.12, 105.76, 53.82, 37.49, 26.56, 17.64. HRMS (EI) m/z calculated for $C_{19}H_{18}NOF$ $[M]^+$ 295.1372, observed 295.1372.

(*R*)-3-Allyl-1,1'-dimethyl-3,3'-biindolin-2-one (3t). White solid, 94% yield. $[\alpha]^{27}_D$ = 182.19 (c = 1, $CHCl_3$), 86% ee [Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, t_R = 11.26 min (minor) and 30.88 min (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.23-7.20 (m, 2H), 7.14-7.09 (m, 2H), 7.04 (d, *J* = 7.5, 1.0 Hz, 1H), 6.98 (s, 1H), 6.93-6.89 (m, 2H), 5.51-5.40 (m, 1H), 5.06-4.90

(m, 2H), 3.71 (s, 3H), 3.24 (s, 3H), 3.19-3.06 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.49, 144.02, 137.80, 132.64, 128.32, 127.71, 126.16, 124.78, 122.69, 121.93, 120.76, 119.42, 119.18, 113.60, 109.54, 108.16, 52.71, 41.05, 33.02, 26.53. HRMS (EI) m/z calculated for $C_{21}H_{20}N_2O$ $[M]^+$ 316.1576, observed 316.1578.

(*S*)-3-Allyl-1,3-dimethyl-5-methoxyl-indole-2-one (3u).[4c] Colorless oil, 92% yield. $[\alpha]^{25}_D$ = -32.43 (c = 1, $CHCl_3$), 70% ee [Chiralpak IB column, *n*-hexane/*i*-PrOH = 98:2, 0.5 mL/min, t_R = 19.02 min (major) and 24.06 min (minor)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80-6.69 (m, 3H), 5.49-4.38 (m, 1H), 5.00-4.89 (m, 2H), 3.78 (s, 3H), 3.15 (s, 3H), 2.53-2.43 (m, 2H), 1.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.04, 156.15, 136.98, 135.28, 132.76, 118.87, 111.84, 110.96, 108.27, 56.04, 48.88, 42.65, 26.40, 22.99. HRMS (EI) m/z calculated for $C_{14}H_{17}NO_2$ $[M]^+$ 231.1259, observed 231.1258.

(*R*)-3-Allyl-3-(3,5-dimethylphenyl)-1-methylindolin-2-one (3v). Colorless oil, 94% yield. $[\alpha]^{27}_D$ = 102.33 (c = 1, $CHCl_3$), 84% ee [Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 98:2, 0.5 mL/min, t_R = 16.24 min (major) and 17.77 min (minor)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.09 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.94 (s, 3H), 6.88-6.86 (m, 2H), 5.41-5.30 (m, 1H), 5.03-4.87 (m, 2H), 3.19 (s, 3H), 3.00 (d, *J* = 6.5 Hz, 2H), 2.24 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.37, 144.05, 139.66, 138.18, 132.79, 132.31, 129.30, 128.27, 125.28,124.94, 122.65, 119.19, 108.30, 56.55, 42.08, 26.54, 21.68. HRMS (EI) m/z calculated for $C_{20}H_{21}NO$ $[M]^+$ 291.1623, observed 291.1624.

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Curriculum Vitae

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